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Valorisation of waste materials using pyrolysis

Master's thesis

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Declaration

I hereby declare that I have authored this master's thesis carrying the name "Valorisation of waste materials using pyrolysis" independently under the guidance of my supervisor. Furthermore, I confirm that I have used only professional literature and other information sources that have been indicated in the thesis and listed in the bibliography at the end of the thesis. As the author of the master's thesis, I further state that I have not infringed the copyrights of third parties in connection with its creation.

In Prague on 19th April 2024

Chhorth Chhiengputheavy

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Valorization of waste materials using pyrolysis

Summary:

The environment is threatened by the overuse of synthetic pesticides and fertilizers. Nonetheless, variety of waste materials such as biomass ash (BA), sewage sludge (SS), plant residues, and by-products such as flue gas desulfurization gypsum (FGDG), and phosphogypsum (PG) are capable of being valorized and restoring plant nutrients. The use of these materials on agricultural land is fraught with danger due to the potential presence of hazardous substances like heavy metals, pathogens, organic and inorganic compounds, and pharmaceuticals that could endanger the environment.

This experiment involved co-pyrolyzing a mixed sample of feedstock material in different proportions and were labeled as TA (SS+BA+FGDG), TB (SS+BA+FGDG+PG), and TD (SS+BA+PG). The pyrolysis was carried out at two different temperatures 500°C and 900°C, with the focus on producing an innovative recycled PSK-fertilizer product. The study evaluated the total and available content of specific group of elements, including potential toxic elements (As, Cd, Cr, Pb), macronutrients (Ca, K, Mg, P, S), and micronutrients (Cu, Fe, Mn, Ni, Zn), to determine the impact of co-pyrolysis treatment. Additionally, pH content and biochar yield were also measured.

The biochar yield and the pH level of the biochar was influenced by increasing the temperature. At 500°C, the pH value was 9, but it increased to between 11 and 12 at 900°C. The biochar yield decreased as the temperature increased to 900°C, TA exhibited the greatest biochar yield at 500°C (71%) and at 900°C (47%). The total and available content of potential toxic elements was influenced by increased temperatures, the total content was lower at 500°C for As and Cr (19 mg/kg and 45 mg/kg, respectively). The availability of potential toxic elements was observed to decrease with pyrolytic temperature especially for As. For instance, the available content of As was found to be below limit of detection for all co-pyrolysis mixtures at 900°C. The temperature had an influence on other elements such as Cd and Cr causing them to decrease as well at 900°C. On the other hand, the total content of P was increased with temperature, reaching a maximum value of 56 g/kg in TD at 900°C. The highest total content of K and S were also reported to be higher in 900°C (84 g/kg and 95 g/kg) respectively. Conversely, the available content of P, K, and S was higher at 500°C, with 4.9 g/kg for P, 70 g/kg for K and 64 g/kg for S in co-pyrolytic mixture TA. In contrast, the available content of feedstocks exhibited a decrease value of Ca, K, P, S, and Zn as the temperature increased. However, Cu and Ni remained below limit of detection at 900°C.

This investigation demonstrated that the co-pyrolytic mixture and temperature increase during pyrolysis has influenced the content of both total content and availability content of the elements.

Keywords: co-pyrolysis; biomass ash; flue gas desulfurization gypsum; phosphogypsum; sewage sludge

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LIST OF ABBREVIATIONS

SS	Sewage sludge
BA	Biomass ash
FGDG	Flue gas desulfurization gypsum
PG	Phosphogypsum
DM	Dry matter
MW	Megawatt
BDL	Below detection limit
TA	Mixture A
TB	Mixture B
TD	Mixture D
As	Arsenic
Cr	Chromium
Cd	Cadmium
Pb	Lead
Ca	Calcium
K	Potassium
Mg	Magnesium
P	Phosphor
S	Sulfur
Cu	Copper
Fe	Iron
Zn	Zinc
Mn	Manganese
Ni	Nikel
C	Carbon
H	Hydrogen
N	Nitrogen

1 Introduction

In the present agricultural system, challenges such as food shortages, energy crises, and environmental pollution persist. The excessive use of synthetic fertilizers and pesticides poses a threat to ecological balance. However, various waste materials such as biomass ash (BA), sewage sludge (SS), plant residues, and by-products such as flue gas desulfurization gypsum (FGDG), and phosphogypsum (PG) are capable of being valorized and can provide recycling of plant nutrients through organic waste recycling, and gained significant importance in maintaining soil health, minimizing pollution, and providing employment prospects. Recognized as a strategy, organic waste recycling is an effective way to promote sustainable agriculture and meet nutrient requirements in various fields, including crop production, horticulture, forest, and aquaculture (Chatterjee et al., 2017).

In the year 2020, the European Union produced an estimated 8.7 million tons of dry matter of sewage sludge annually (Vávrová et al., 2023). The composition and properties of wastewater sludge depend primarily on wastewater characteristics and treatment method (Zaker et al., 2019). After biomass materials (plant residues, wood, and other organic matter) are burned, biomass ash remains and contains macro elements such as P, K, Ca, and S (Zajac et al., 2018). PG composed mainly by $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is a major waste from the phosphate fertilizer industry (Vimal et al., 2022a), and annually more than 85% of PG in the world is dumped as waste (Tayibi et al., 2009). However, PG as fertilizer has been used for decades due to its content of plant and soil supplements such as Ca, P, and S (Hentati et al., 2015). According to the American Coal Ash Association, FGDG produced in 2021 was 77.3 million MT, and it has potential benefit supplies of nutrients Ca and S to plants and application of soil amendment (Panday et al., 2018).

There is a significant concern associated with the use of these materials on agricultural land regarding the potential hazards associated with toxic contaminants, such as heavy metals, pathogens, and pharmaceuticals, that pose potential risk to the environment which are restricted for agricultural use (Baligar et al., 2011; Zaker et al., 2019).

One potential method for variolization is pyrolysis, which is a thermal treatment process involving heating the waste materials to high temperatures in the absence of oxygen (Kan et al., 2016). Pyrolysis temperature plays a crucial role in changing the behaviour of heavy metals in pyrolysis products (Gong et al., 2018). Through pyrolysis, heavy metals in sewage sludge can be kept and concentrated in biochar (Yang et al., 2021a).

Biochar derived from sludge, however, ought not to be directly utilized in soil-related applications due to the elevated heavy metal content, which may present significant environmental hazards arising from soil and groundwater pollution (Wang et al., 2020). Consequently, it is imperative to develop and explore alternative technologies that can effectively decrease the heavy metal presence within sludge-derived biochar. Co-pyrolysis is an innovative environmental technology that can decrease heavy metal contents in the resulting biochar (Wang et al., 2022). Co-pyrolysis involves combining two or more distinct materials as

the feedstock. The major advantage of using the co-pyrolysis method is the significant reduction in waste volume as more waste is utilized as feedstock. Additionally, this method helps in minimizing landfill requirements, reducing waste treatment costs, and addressing various environmental issues (Abnisa & Daud, 2014).

The use of nutrient-enriched biochar has increased recently to enhance and balance the nutrient supply to plants (Fachini et al., 2022). Biochar impacts nutrient cycling in soils by retaining and sorbing nutrients thus affecting their bioavailability. Biochar-based fertilizer resulted in the highest crop productivity increases in soils with initially high fertility and low response to conventional fertilizers (Melo et al., 2022).

The aims of this Diploma thesis will be to analyse co-pyrolysis of four different waste materials such as sewage sludge, biomass ash, flue gas desulphurization gypsum and phosphogypsum at temperatures 500°C and 900°C with a focus on producing an innovative recycled PKS-fertilizer product.

2 Scientific hypothesis and aims of the thesis.

Objective of the study:

- To evaluate the effect of pyrolytic temperature on the total contents of elements in the biochar produced by co-pyrolysis of SS, BA, FGDG and PG
- To evaluate the effect of pyrolytic temperature on the available contents of elements in the biochar produced by co-pyrolysis of SS, BA, FGDG and PG

Hypothesis:

1. The total content of the elements in biochar is dependent on both temperature, and feedstock composition. Thus, is presumed that the behaviour of the individual elements will differ between tested mixtures.
2. The availability of the elements in biochar is affected by both the pyrolysis temperature and composition of pyrolytic mixture.
3. The losses of potentially toxic elements during pyrolysis and ash content in the biochar are affected by the pyrolysis temperature and the pyrolytic mixture and is not proportional to the feedstock materials pyrolyzed alone.

3 Literature research

3.1 Sewage sludge production

Sewage sludge is a by-product of wastewater treatment, coming from several sources such as domestic sewage, industrial waste, and storm water runoff from roads and other paved surface. Sewage sludge is produced during the separation of solid waste from liquid effluent during wastewater treatment by processed through physical, biological, and/or chemical processes. Sewage sludge, which is rich in organic matter and plant macronutrients include Nitrogen (N), Potassium (K), Calcium (Ca), Magnesium (Mg), Phosphorus (P) and Sulphur (S) and micronutrients include Iron (Fe), Zinc (Zn), Manganese (Mn), Copper (Cu), Boron (B), Chlorine (Cl), Molybdenum (Mo) and Nickel (Ni), has the potential to enhance soil qualities, through its use as fertilizer or soil conditioner for pasture, horticultural plants, food crops, and vegetable crops (Khalid U, 2012) (Joseph S. Mtshali, 2014).

Figure 1 illustrates the production of sewage sludge in some European countries. In addition, Germany produces the greatest amount of sludge, followed by the United Kingdom and France. Additionally, Spain and Italy produce over 500000 tons of dry matter each year. There are estimates that these five nations produced 75% of the sewage sludge in Europe (Kacprzak et al., 2017).

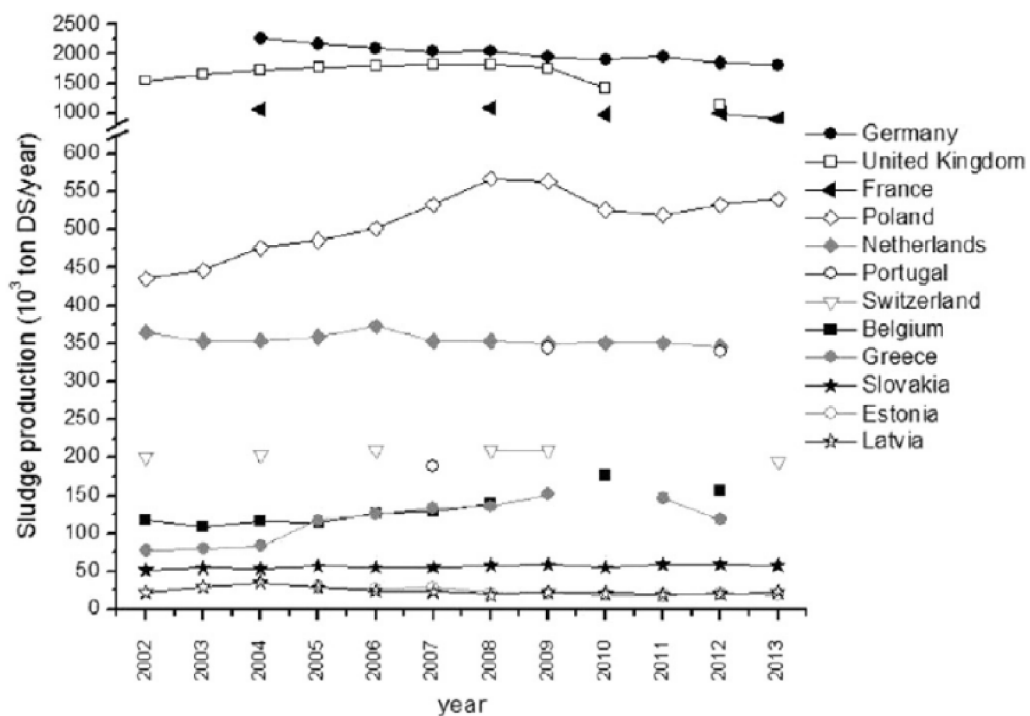


Figure 1. Sewage Sludge production in some countries of the EU (Kacprzak et al., 2017)

Sewage sludge production is a significant environmental issue that concerns public health and the sustainability of resources when these substances are released into the environment such as through the widespread use of biosolids as fertilizers in agriculture practice. It contains a variety

of contaminants, including heavy metals, organic compounds, and pathogens, that can be harmful to human health if not properly managed. The EU considers the reuse of sludge as a long-term solution while the regulations set forth requirements for the proper management of toxic heavy metal and nutrient content of sewage sludge, including requirements for testing and monitoring, to ensure that the sludge does not contain unsafe levels of contaminants (Díaz-Cruz et al., 2009).

The restrictions currently governing in European Union about the use of sewage sludge in agriculture is the limit values for heavy metal such as Cadmium (Cd), Copper (Cu), Nickel (Ni), Lead (Pb), Mercury (Hg), Chromium (Cr) and Zinc (Zn) listed in Council Directive of 12 June 1986 on the protection of the environment (86/278/EEC). The sewage sludge Directive seeks to regulate the use of sewage sludge in such a way as to prevent harmful effects on soil, vegetation, animals, and man and to ensure the appropriate use of sewage sludge in agriculture (Hudcová H., 2019).

3.1.1 Sewage Sludge Composition

The characteristics of sewage sludge are generally varied, and it contains organic and inorganic chemicals, metals, and pathogens. It is regarded as a valuable resource due to its application as an amendment to soil, a source of energy, and as a nutrient source. As part of its physicochemical characteristics, sewage sludge consists of 20% fat, 50% carbohydrates (sugar, starch, fiber), 30% to 40% organic matter, 3% nitrogen, 1.5% phosphorus, 0.7% potassium, 10 % to 20 % ratio of C/N, and high levels of heavy metal ions. According to the report, dry sludge has a heat value of approximately 12.000 kJ/kg, and a pH of between 6.5 and 7 (Kumar et al., 2017).

Most sewage sludge contains heavy metals such as cadmium, copper, nickel, lead, zinc, mercury, and chromium. In table 1 provides information regarding the mean content of potential toxic elements in sewage sludge, measured in milligrams per kilogram of dry matter (mg/kg DM), for various countries, including European union member states, India, China, the UK, and Japan. These heavy metals are regarded as toxic and potentially harmful elements. During the primary and secondary treatment processes, the metals become concentrated in the sludge as a result of their association with solids that can be settled. Utilizing sewage sludge for agricultural purposes effectively recycles the nutrients found within, making it a valuable resource for sustainable farming. However, the presence of pollutants, such as heavy metals, organic compounds, pharmaceuticals, and pathogens, poses a challenge when applying sewage sludge to agricultural land. These contaminants may be removed from the soil through processes like plant absorption, wind, and water erosion, leaching, and runoff (Usman et al., 2012).

Table 1. The content of heavy metals in sludge in different countries

Source		Elements (mg/kg DM)					
		Pd	Cu	Zn	Cd	Cr	Ni
(Usman et al., 2012)	EU member states	13 - 221	39 - 361	142 - 2000	0.4 - 3.8	16 - 275	9 - 90
	India	26 - 154	-	-	2 - 9	66 -1098	12 - 596
(Milik et al., 2017)	China	69.33	1467.13	7026.66	36.81	210.35	214.29
	UK	221.5	562	778	3.5	159.5	58.5
(Kumazawa, 1997)	Japan	53	255	979	2.3	69	40

3.1.2 Sewage Sludge treatment

Sewage sludge treatment is a crucial aspect of municipal wastewater management that requires attention due to the pollution potential of untreated sludge. However, techniques for sewage sludge treatment such as anaerobic digestion, composting, and incineration are essential to ensure the quality of wastewater. There are three main techniques of treatment: pre-treatment, primary treatment, secondary treatment, and tertiary treatment. Primary treatment produces sludge with a high content of suspended solids, while secondary treatment produces sludge with higher levels of biodegradable organic matter. Finally, tertiary treatment produces sludge with a lower content of suspended solids and a higher content of dissolved solids. These techniques reduce the levels of organic pollutants, suspended solids, and pathogenic microorganisms that are present in the sludge. They also reduce the offensive odour and help to stabilize the sludge and reduce its volume. Sewage sludge produced during the wastewater treatment process must be treated carefully before being discharged back into the environment (Demirbas et al., 2017).

As part of the further treatment process, numerous stabilization techniques are used such as aerobic and anaerobic digestion, alkaline stabilization, composting, and heat drying. These techniques enhance the quality and beneficial uses of sludge, especially for land application and other purposes (Beshah, 2010).

3.2 Biomass Ash Production

Biomass ash is a by-product of the combustion of biomass, such as wood, sewage sludge, agricultural residues, and other organic materials, and has recently gained attention due to its potential applications in various industries (Knapp & Insam, 2011). Approximately 480 million tons of ash are generated every year worldwide from thermochemical processing of biomass (Vassilev et al., 2013). Biomass ash can contribute to soil remediation, long-term nutrient supply, and carbon sequestration in the most ecological and sustainable disposal method. The used of biomass in agriculture and construction, electrical, as well as industries: glass, rubber,

ceramic, and zeolite manufacturing and adsorption (as a source of silica/zeolites) (Trivedi et al., 2016).

In order to convert biomass into bioenergy, various technologies can be used including combustion, torrefaction, pyrolysis, and gasification. Combustion is the most widely used process to convert biomass into energy, by burning the material to produce heat. In figure 2 shown the diagram of combustion of biomass (Kundu et al., 2018), combustion of biomass is the simplest method of thermal processing (Stankowski et al., 2021). It is important to note that all these processes have a common basis in the decomposition of thermal energy, which can yield a wide range of products, including solids, liquids, and gases (Kundu et al., 2018).

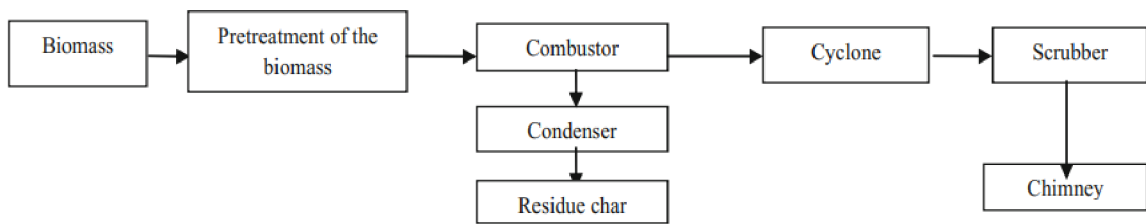


Figure 2. Flow diagram of combustion of biomass (Kundu et al., 2018)

3.2.1 Biomass Ash composition

Ash produced by biomass combustion has a wide variety of chemical compositions such as silicon, aluminum, iron, calcium, magnesium, sodium, potassium, titanium, and manganese, with heavy metals as impurities. Ash from all types of biomasses should, however, be evaluated individually based on its chemical composition and the biomass's origin. In qualitative analyses of the distribution of macro-elements in ash according to the combusted plants, it was discovered that calcium > potassium > phosphorus were the most abundant elements in hardwood ash, whereas calcium > silicon > potassium were the most abundant elements in conifer ash. For straw ash, potassium is the most abundant element followed by calcium, chlorine, and phosphorus, while for grass straw ash, calcium is the most abundant element followed by potassium, calcium, and chlorine. According to the analysis of ash composition, the following elements were identified: Si, Al, Ca, K, Na, Mg, Fe, P, Ti, CaO, SiO₂, K₂O, MgO, P₂O₅ and Al₂O₃ are the main compounds found in ash. (Zajac et al., 2018). The chemical composition of ash is presented in Table 2.

Table 2. Chemical composition of biomass ash (Wójcik et al., 2017)

Compound	Value (mass%)
CaO	45.64
SiO ₂	15.17
K ₂ O	9.78
SO ₃	7.58
P ₂ O ₅	4.59
MgO	4.25
Al ₂ O ₃	4.14
Fe ₂ O ₃	3.85
MnO	1.61
ZnO	0.37
Na ₂ O	0.2

3.2.2 Biomass Ash in Agriculture

As biomass ash is composed of plant-growing nutrient and essential elements present as macronutrient, micronutrient and trace elements that are suitable and influence on soil, it contributes to better plant growth and yields (Demeyer et al., 2001; Vassilev et al., 2013). Due to their porous nature, ashes also enhance the soil's water-holding ability, texture, and level of exchangeable K, Ca, Mg, P, and Mn ions, improves soil properties like aeration at the crop root zone (Trivedi et al., 2016). In acid soils, ash is often used as a liming agent due to its alkaline properties (Odlare & Pell, 2009). Additionally, low acidic leaching from soil to water stream results in less mobilization and bioavailability of hazardous elements, which enhances biological activity and better environment to some microorganisms (Vassilev et al., 2013).

It is important to avoid soil application of BMAs from cyclone separators, filter fly ashes, and semi-biomass ashes. These materials are often contaminated with hazardous trace elements such as As, B, Ba, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Se, and Zn, so they must not be used for soil applications (Trivedi et al., 2016).

The potential application of Fly Ash with added organic and inorganic materials has different degrees of soil improvement. Several other organic and inorganic amendments, including lime, gypsum, red mud, poultry manure, sewage sludge, composts, press mud, vermicompost, biochar, bioinoculants, etc., have been used in conjunction with fly ash to further enhance the soil quality and increase plant biomass production through physical, chemical, and biological enhancements. Figure 4 summarizes the details associated with the co-application of fly ash with these materials (Ram & Masto, 2014).

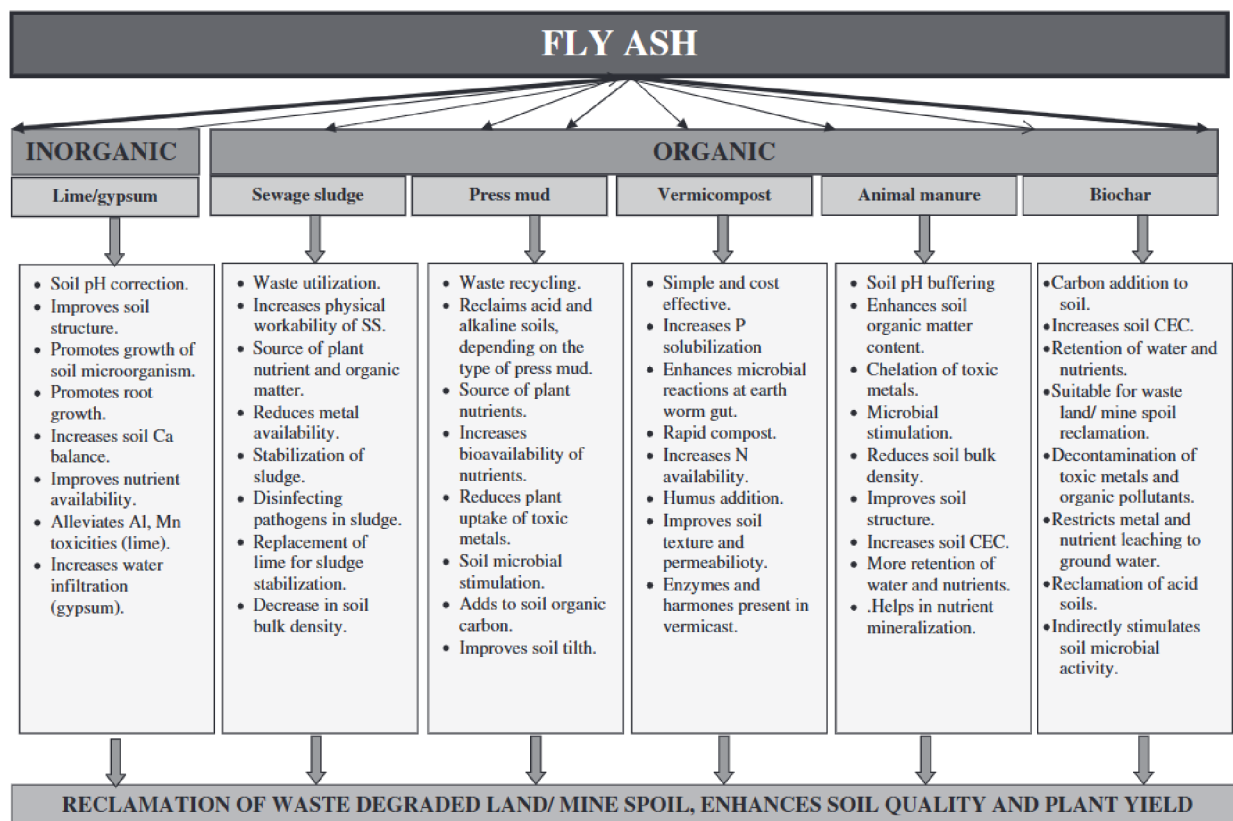


Figure 4. Beneficial role of inorganic and organic amendments used along with fly ash (Ram & Masto, 2014)

3.3 Flue gas desulfurization gypsum

There are a variety of residues generated during the coal combustion process, including fly ash, bottom ash, boiler slag, flue bed combustion ash, including flue gas desulfurization gypsum (FGDG). Flue gas desulfurization gypsum, commonly referred to FGD gypsum or FGDG, emerges as a by-product of the flue gas desulfurization process used in coal-fired power plants. It is estimated that coal for energy production contains up to 2.5% Sulfur. The flue gas desulfurization (FGD) of one power plant block can produce up to 20 tons of gypsum per hour (Tesárek et al., 2007). Additionally, the amount of beneficially used FGDG has decreased over the past decade, while its production has increased dramatically. Production rates of FGDG increased from 11 million metric tons in 2006 to 29 million MT in 2016, with utilization rates decreasing from 79% to 57% (Koralegedara et al., 2019).

FGDG is produced when sulphur dioxide is removed from flue gases, the resulting FGDG is a combination of gypsum and other impurities such as ash, calcium, carbonate and Mg, K, Na, Al, etc., (Wang & Deng, 2015) and it is created as a solid form of calcium sulphate. This type of gypsum can be recycled and used in a variety of beneficial applications such as a soil amendment, in cement and plaster products, and even in construction materials due to its abundance, chemical and physical properties (Koralegedara et al., 2019).

3.3.1 Flue gas desulfurization gypsum production

During coal combustion, flue-gas desulfurization materials (FGDs) are solids that are produced by removing SO₂ from exhaust gases before the gases are released into the atmosphere. The United States generates more than 60 million tons of FGD materials each year (Butalia et al., 2017).

The process of flue gas desulfurization (FGD) can be classified into two main types of processes: once-through or regenerable processes depending on how the sorbent is treated after SO₂ adsorption. The sorbent of once-through, or non-regenerable, processes can be utilized or disposed of as a waste product. However, regenerable processes allow sorbed SO₂ to be released into other products such as elemental S, H₂SO₄, or liquid SO₂. Figure 5 presented classification of flue gas desulphurization processes (Pandey et al., 2005).

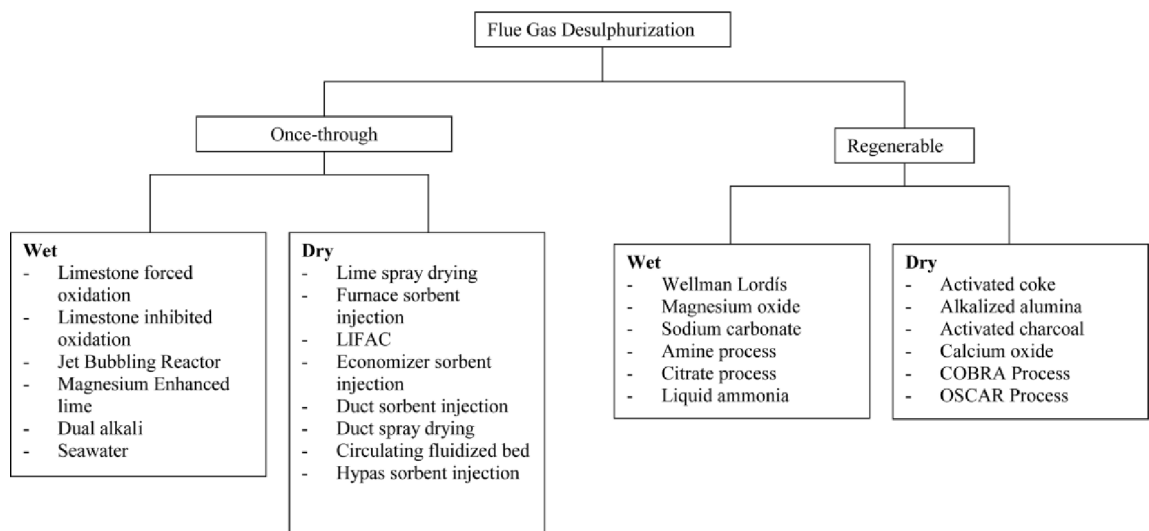
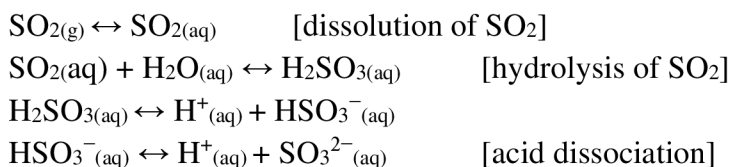


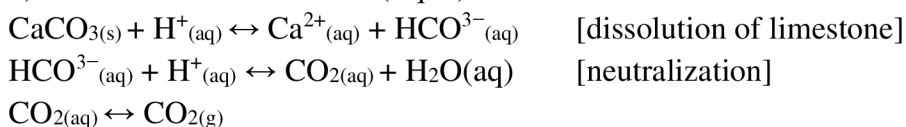
Figure 5. Classification scheme of flue gas desulfurization technologies (Pandey et al., 2005)

One of the most common FGDG methods is limestone-based wet scrubbing. The chemical reactions at work are summarized below in reaction of Eq. 1 and Eq. 2 (Córdoba, 2015; Koralegedara et al., 2019):

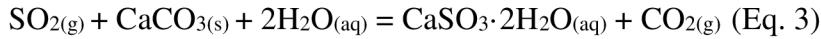
1) SO₂ in flue gas (Eq. 1)



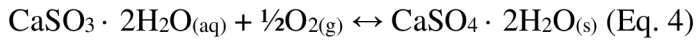
2) Dissolution of limestone (Eq. 2)



An overall chemical reaction of the above processes, which occurred in the FGD system is given below (Eq. 3):



The produced calcium sulphite ($\text{CaSO}_3 \cdot 2\text{H}_2\text{O}$) is then oxidized, resulting in FGDG (Eq. 4).



3.3.2 Composition of FGDG

FGD gypsum also has some properties such as attached water about 8%~12%, relatively concentrated particle sizes, with diameters between 30-60 μm , and a pH of approximately 5-9. Moreover, the physical properties and chemical composition of FGDG are quite different from natural gypsum. Compared to natural gypsum, there are differences in color, polymorph, particle size, and impurities, but the chemical composition is very similar, and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ of FGD gypsum is overall greater (Wang & Deng, 2015).

Flue gas desulphurization gypsum contains calcium sulphate (CaSO_4) as the main component, but it may also contain Mg, K, Cl, F, B, Al, Fe, Si, and Se. In addition, toxic elements such as, Hg, Cd, and Pb may be found in trace amounts, which are determined by the composition of the combusted coal along with the limestone, lime, and other additives used in the FGD process (Koralegedara et al., 2019). its chemical composition encompasses a range of elements, notably Silicon dioxide (SiO_2), Carbon (C), Aluminium oxide (Al_2O_3), Iron oxide (Fe_2O_3), Calcium oxide (CaO), Magnesium oxide (MgO), Potassium oxide (K_2O), Sodium oxide (Na_2O), and Silicon dioxide (SiO_2) (Li & Wang, 2019). In the table 3 provides the chemical composition of Flue Gas Desulfurization Gypsum from various sources.

Table 3. Chemical composition of FGDG

Source	Chemical composition of FGDG, mass %		
	(Li et al., 2015)	(Li & Wang, 2019)	(Telesca et al., 2013)
SiO ₂	2	0.8 - 7.2	3.3
Al ₂ O ₃	1.2	0.3 - 3.7	1
CaO	28.1	25.0 - 50.0	31.9
K ₂ O	0.1	0.1 - 0.3	-
Na ₂ O	0.3	0.01 - 0.3	-
Fe ₂ O ₃	0.5	0.1 - 0.9	0.3
SO ₃	40.8	24.0 - 54.7	36.9
MgO	1	0.04 - 3.80	3.8
P ₂ O ₅	<dl	0.01	0.01
MnO	0.01	0.01	-
TiO ₂	0.07	0.05 - 0.07	0.05

<dl, under detected limit.

3.3.3 FGDG in agriculture

According to the American Coal Ash Association (ACAA, 2021), coal combustion in power plants generates coal combustion residues about 77.3 million tons which is 6 million tons more than the previous year (69.1 million tons in 2020). A total of 46.5 million tons of coal combustion products have been beneficially utilized in 2021, including fly ash, bottom ash, flue gas desulfurization material, and flue bed combustion ashes.

A potential benefit of FGDG is that it supplies nutrients Calcium and Sulphur to plants, reclaiming sodic soils, mitigating subsoil acidity and Aluminum (Al) toxicity, improves soil physicochemical properties by promoting aggregation and increasing infiltration rate and movement through soil profile, reduces soil and nutrient Phosphor losses, making it a more economical source of gypsum (Panday et al., 2018).

FGDG may be useful as an amendment to enhance plant growth and boost crop yield for agricultural soils because it is a rich source of Ca and S and possible that it also contain sodium Chloride (NaCl), Magnesium oxide (MgO), Calcium chloride (CaCl₂), Phosphoric oxide (P₂O₅), CaCO₃, Silicon dioxide (SiO₂) and other by-products such as fluorine (fluoride compounds) (Panday et al., 2018). When coal is burned and SO₂ is removed from the flue gases, flue gas desulfurization products may be an efficient source of Sulfur. Many crops require Sulfur fertilization. When applied to agricultural soils, FGD products can supply plants with the needed Sulfur and increase alfalfa and soybean yields (Chen et al., 2005). Some generalizations can be made regarding soil physicochemical properties after FGDG application. The mechanisms and effects of various degraded soils reclaimed by FGDG are shown in Figure 6 (Wang & Yang, 2018).

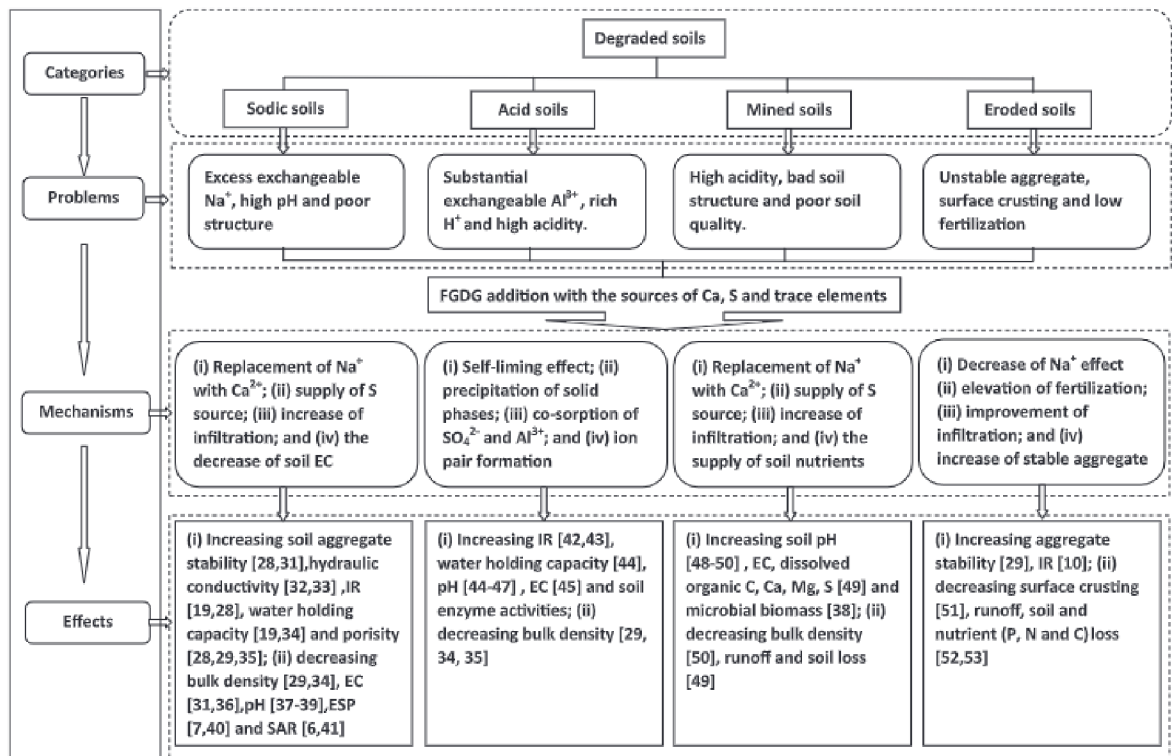


Figure 6. Mechanisms and effects of degraded soil reclaimed by FGDG (Wang & Yang, 2018).

3.4 Phosphogypsum

Phosphogypsum (PG) is an industrial by-product created when phosphoric acid is produced from natural phosphate rock using the wet process. Phosphate ore is processed using either dry thermal or wet acid techniques to create phosphoric acid. As shown in figure 7 is a general scheme of the processes of each technique. Phosphorus is made using the dry thermal process in an electric arc furnace. The "wet process," also known as the wet chemical phosphoric acid treatment process, is frequently used to create calcium sulphate and phosphoric acid, mostly in the form of dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (Eq. 5) (Tayibi et al., 2009).

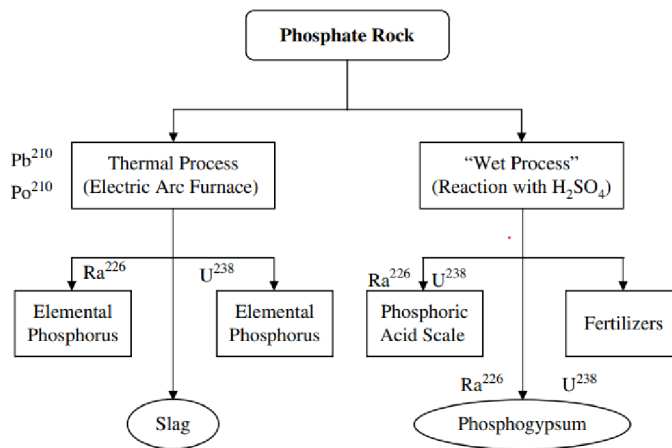


Figure 7. A general scheme of the phosphor gypsum processes (Tayibi et al., 2009)

The amount of phosphogypsum produced annually about 200 million tonnes (Fuleihan, 2012). More than 85% of the PG generated each year is dumped on land or at sea, creating unsolvable and troublesome problems. Environmental issues are associated to the large PG stockpiles and their adverse effects on surrounding land, water and air (Tayibi et al., 2009). The main factors that make this material problematic for storage and disposal, as well as limiting its use in the construction and agricultural industries, are the presence of toxic trace elements and the radioactivity of Radium (Ra) and Uranium (U) (Papanicolaou et al., 2009).

3.4.1 Phosphogypsum Composition and properties

PG is a powdery material with little or no plasticity and is considered an acidic by-product due to the residual phosphoric, sulphuric, and hydrofluoric acids ($\text{pH} < 3$). Phosphate rock particle size typically ranges from 0.250 to 0.045 mm, depending on the reactor condition and the source of the phosphate rock. Furthermore, the composition of PG are components include CaO , SO_3 , SiO_2 , Al_2O_3 , Fe_2O_3 , P_2O_5 , and F, as well as trace metal content (arsenic, silver, barium, cadmium, chromium, lead, mercury, and Selenium). Also, PG is generally high in Ag, Au, Cd, Se, Sr, and some rare earth elements such as Y (yttrium) (Tayibi et al., 2009).

3.4.2 Phosphogypsum in agriculture

In many parts of the world, phosphate fertilizer has been used for decades as an agricultural fertilizer. PG has been applied to agricultural soils as a Calcium, Phosphorus, and Sulphate supplement. This has been done to improve crop production and recover acidic soils by reducing Al-toxicity and sodic soils. Furthermore, it was used to prevent runoff and erosion in agricultural soils exposed to heavy rainstorms alone or combined with other synthetic organic polymers (Hentati et al., 2015). Due to its low pH value, it can be used as an additive in other alkaline wastes, to reduce their pH and to improve their properties (Pliaka & Gaidajis, 2022).

3.5 Pyrolysis

Pyrolysis is one of the thermochemical processes used to turn biomass into energy and chemical products like liquid bio-oil, solid biochar, and pyrolytic gas under low-oxygen or anoxic conditions. In figure 8 shown schematic diagram of biomass pyrolysis to biochar and bio-oil. Biomass pyrolysis can be divided into three main categories: slow pyrolysis (conventional), fast pyrolysis, and flash pyrolysis depending on the heating rate and residence time (Kan et al., 2016). These categories are primarily focused on maximizing the yields of either bio-oil or biochar. The biomass pyrolysis procedure, yields, and product characteristics are influenced by several factors. These include the kind of biomass, the physical, chemical, and biological pre-treatment of the biomass, the reaction environment, temperature, heating rate, and vapour residence time. (Frišták et al., 2018). Table 4 presented the summarize the operating condition and the yield of the product depends on different pyrolysis type (Panchasara & Ashwath, 2021).

The pyrolysis of biomass is accepted to involve three main stages: I initial free moisture evaporation, (ii) primary decomposition, and (iii) secondary reactions (oil cracking and repolymerization) (White et al., 2011).

Table 4. Outcomes of pyrolysis obtained from various pyrolysis technologies (Panchasara & Ashwath, 2021)

Pyrolysis	Operating Conditions	Product Yield
Slow Pyrolysis	Temperature: 300-700 °C Vapor residence time: 10-100 min Heating rate: 0.1-1 °C/s Feedstock size: 5-50 mm	Bio-oil: ~ 30%wt Biochar: ~35%wt Gases: ~35%wt
Fast Pyrolysis	Temperature: 400-800 °C Vapor residence time: 0.5-5s Heating rate: 10-200 °C/s Feedstock size: 3 mm	Bio-oil: ~50%wt Biochar: ~ 20%wt Gases: ~30%wt
Flash Pyrolysis	Temperature: 800-1000 °C Vapor residence time: 0.5 s Heating rate: 1000 °C/s Feedstock size: 0,2 mm	Bio-oil: ~75%wt Biochar: ~12%wt Gases: ~13%wt

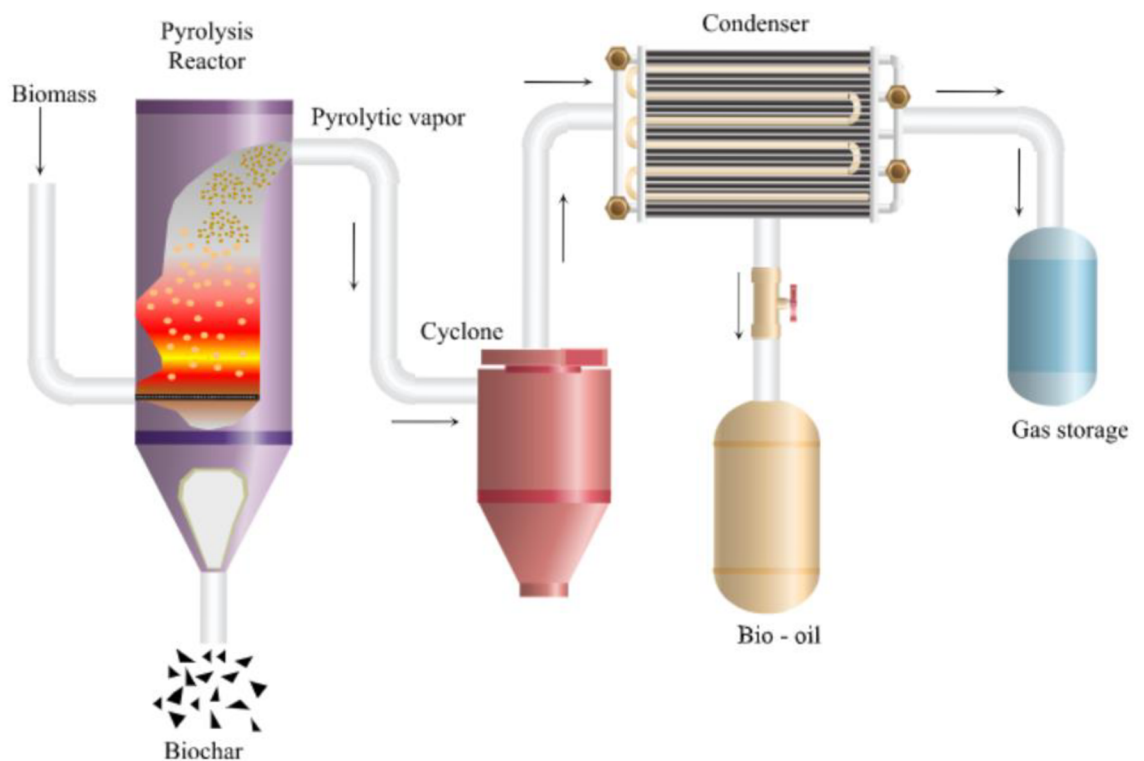


Figure 8. Schematic diagram of biomass pyrolysis to biochar and bio-oil (Yogalakshmi et al., 2022)

3.5.1 Pyrolysis temperature

The distribution and characteristics of the products are significantly influenced by the pyrolysis temperature. Temperature is one of many process variables that largely determines the yield and quality of biochar. Biochar yields are negatively affected by increasing the temperature during pyrolysis. As the higher the temperature, the more thermally cracked heavy hydrocarbon materials become, resulting in more liquids and gases, and a decrease in biochar yield. Biochar formed during the primary pyrolysis reaction undergoes secondary reactions at high temperatures, increasing liquids and gaseous products while reducing solid char production. Low temperatures are ideal for high biochar yields. This is because at high temperatures, the energy given to the biomass may exceed the bond cessation energy. This lets the biomass release its volatile components. As a result of these volatile constituents of biomass, less char is produced (Tripathi et al., 2016).

The bio-oils and char products turn into gas at temperatures above 600°C as result of the predominate secondary cracking reactions (Li et al., 2007). Temperatures between 300°C and 500°C and 600°C and 800°C enhance the polar, aliphatic, and aromatic fractions in the bio-oils. The decarboxylation and dehydration reactions that occur at temperatures above 700°C typically result in an increase in the carbon content of bio-oils in the form of polycyclic aromatic hydrocarbons (PAHs), such as pyrene and phenanthrene (Kan et al., 2016).

3.6 Co-pyrolysis

Co-pyrolysis involves the use of two or more different materials as feedstocks (agricultural residues, wood residues, municipal solid wastes, and dedicated energy crops), conducted at moderate operating temperatures without oxygen in a closed reactor system. This creates synergies which can significantly increase energy and yield output. In table 5 provide the results of co-pyrolysis experiments involving sewage sludge and different materials, method, and however, co-pyrolysis techniques have the potential to be more profitable than pyrolysis of the biomass alone. The main advantage of co-pyrolysis is that a significant amount of waste can be consumed as feedstock, reducing waste volume significantly. As well as reducing the need for landfills, it reduces the cost of waste treatment and solves several environmental problems. Waste disposal in landfills is undesirable, so this method can be proposed as an alternative waste management procedure that will reduce waste effectively and enhance energy security (Abnisa & Wan Daud, 2014).

Table 5. Co-pyrolysis of sewage sludge and different material

Source	Method	Relevant result
Vamvuka & Sfakiotakis, 2019	thermogravimetric analysis of swine sludge, olive kernel & olive pruning included mixtures with 10%, 30% & 50% sludge ratios, temperature range of 25-900°C, conducted at heating rates: 5, 10, 20, 30, and 40°C/min, with airflow rate 35 ml/min.	Heavy metals As, Hg, Cd, and Co were at low levels (<0.4 ppb), Pb ranged from 1.8 to 7.3 ppm. The ashes have potential applications in secondary construction, road building, liming agents, and fertilizers when combined with other byproducts.
Liu et al., 2017a	sewage sludge and walnut mixture of 4:1 ratio, Co-pyrolysis temperature 500°C, heating rate: 10 °C/min & maintained for 1h.	Co-pyrolysis influenced the reducing toxicity and risk of heavy metals, which could transform mobile fractions of Cu, Ni, Cd, and Cr to stable fractions.
Wang et al., 2019	co-pyrolyzing sewage sludge & cotton stalks, temperature of 650°C for 2h, mixing ratios of cotton stalks to sewage sludge, ranging from 1:9 to 9:1 by weight.	Biochar with lower mixing ratios had more ash, higher CECs, less organic carbon, but more mineral nutrients (N, P, K, Ca, Fe). These mineral nutrients are beneficial for improving nutrient supply and retention in biochar-treated soil.
Vimal et al., 2022b	Co-pyrolysis of Poultry, banana peduncle & PG at 700°C, 10°C/min, 1h. Ratio 1:1:1, 1:2:1, 1:3:1	Biochar mainly showed variations in their K–P–S contents. The banana peduncle-poultry litter-phosphogypsum (1:1:1) derived biochar had higher levels of K (5.1%) and S (11.35%), while, resulting in a P content of 3.84 % in the banana peduncle-poultry litter-phosphogypsum (1:3:1).
Ray et al., 2023	Dried gypsum pond water and treated- gypsum pond water - Biomass were pyrolyzed at 400°C, 600°C and 800 °C with heating rate 10 °C/min and 1 h.	P & S in gypsum pond wastewater (GPW) from the phosphate fertilizer industry can be reclaimed using banana peduncle biomass, producing multi-nutrient-rich (K-P-S) biochar via pyrolysis. These nutrients are retained in the biochar in different mineral phases and are primarily water-soluble.

3.7 Potential toxic element release in co-pyrolysis

During pyrolysis, heavy metals present in sludge are concentrated within the resulting biochar due to the volatilization and conversion of organic compounds into bio-oil and pyrolytic gas. The presence of heavy metals in sewage sludge can contribute to environmental problems and secondary pollution. To address this issue, co-pyrolysis of sewage sludge with other biomass materials can be considered as a potential solution. This co-pyrolysis process not only helps mitigate heavy metal pollution in biochar produced from sewage sludge but also stabilizes bioavailable heavy metals, reducing their direct toxicity in the resulting co-pyrolysis biochar (Yang et al., 2021).

For instance, (Liu et al., 2017) conducted research demonstrating that co-pyrolysis has the ability to transform mobile forms of heavy metals (such as acid soluble/exchangeable and reducible forms) into more stable forms (like oxidizable and residual forms). As a result, the contents of heavy metals like Cu, Ni, Cd, Cr, and Zn in the leachate were lower than the regulatory standards in China. Furthermore, the assessment of environmental risk revealed that co-pyrolysis reduced the risk levels of Cu, Ni, and Cd to a low-risk category, and notably, there was no significant risk associated with Cr in the final product.

3.8 Chemical of PKS-fertilizer

Biochars are valuable soil amendments because they contain a variety of plant nutrients, and they can also help reduce atmospheric carbon by capturing carbon. The biochar produced from different feedstocks contains a diverse range of macronutrients (N, P, K, Ca, Mg, and S) as well as micronutrients (Na, Mn, Cu, Fe, Se, Mo, and Zn). The content of the corresponding nutrient components varies greatly, primarily depending on the type of biomass and the pyrolysis conditions. Due to the loss of biomass mass at higher temperatures during pyrolysis, the contents of nutrient elements in the biochar are increased (Kan et al., 2016). Increased biochar application rates significantly increased soil pH, Phosphorus, Potassium, and Sulfur content (Wang & Wang, 2019).

Natural ecosystems replace P lost through soil-plant cycling with natural processes such as rock weathering or human-managed ecosystems with fertilizers. There are several potential sources of P loss in ecosystems such as soil erosion, soil loss, or leaching. It is one of the primary macronutrients needed for plant growth and health, from seedling to maturity. Furthermore, P plays a crucial role in complex energy transformations, essential for all living organisms, is a vital component of DNA, and is essential for protein synthesis and other compounds (Vali et al., 2023). In several European Union (EU) member states, there is a growing need to reclaim and reuse phosphorus from sewage sludge as a soil fertilizer. While various methods exist for this purpose, pyrolysis conducted at temperatures ranging from 500°C to 800 °C stands out as the most environmentally efficient option (EBI, 2023). The initial release of Phosphorus (P) from biochar composites demonstrates the potential to enhance the germination of plants. Furthermore, the slower P release from these biochar composites offers advantages in terms of

improved nutrient utilization efficiency and reduced nutrient leaching losses (Vimal et al., 2022b).

According to estimates, applying K to the soil only restores around 35% of K from aboveground biomass of crops each year. However, compared to N and P recovery, K recovery has gotten far less attention. Therefore, it is important to evaluate plant K availability following the direct application of biochar and ash to soil as a low-cost recirculation technique (Carey et al., 2016). Sulphur (S) is an essential nutrient for plant growth, with crop requirements like phosphorus. However, for many years, little attention has been given to this element. It is also important to note that an insufficient supply of sulphur can affect yields and quality, since it is a constituent of the amino acid methionine and cysteine as well (Scherer, 2001). The Phosphorus (P) and Sulphur (S) content in gypsum pond wastewater (GPW) from the phosphate fertilizer industry can be effectively extracted using banana peduncle biomass. This extraction process holds the potential to yield multi-nutrient-enriched biochar containing Potassium (K), Phosphorus (P), and Sulphur (S) through pyrolysis (Ray et al., 2023).

4 Materials and methods

4.1 Feedstocks

The sewage sludge sample comes from a wastewater treatment plant in the Czech Republic that has the capacity to serve 29,000 population equivalents. The biosolids were treated through anaerobic stabilization, specifically the mesophilic conventional anaerobic digestion method, and were then dried using a decanter centrifuge. At the time of collection, the biosolids had a dry matter content of 24% by weight (Mercl et al., 2021). The biomass fly ash used in the experiment was acquired from an unnamed commercial power plant that can produce 19.25 MW of power. The power plant burns separated straw bales in a combustion chamber at a temperature of 600°C -700°C, which results in the production of approximately 2000 tons of fly ash per year (Košnář et al., 2020). The sample of flue gas desulfurization gypsum (FGDG) was obtained from a coal-fired power plant located in the Czech Republic. The phosphogypsum (PG), was collected from the Wizów stock located in southwestern Poland. To maintain confidentiality, the producers provided the samples only on the condition of anonymity and are therefore labelled as FGDG and PG (Murillo et al., 2022).

4.2 Experimental Design

Sample mixtures of the experiment is the combination of sewage sludge (SS), Biomass ash (BA), Flue gas desulfurization gypsum (FGDG) and Phosphogypsum (PG) with three different ratios. The materials were mixed in different proportions of SS-BA-FGDG-PG [1:0.3:0.3:0] label as TA, SS-BA-FGDG-PG [1:0.3:0.15:0.15] label as TB, and SS-BA-FGDG-PG [1:0.3:0:0.3] label as TD. Each feedstock and mixtures were pyrolysis under the set of temperature at 500°C and 900°C. All the pyrolysis experiments were done in duplicates. The experimental design is presented in Table 6.

Table 6. Experimental design of feedstocks mixture under set temperature

	Sample Mixture (g)				Temperature of pyrolysis (°C)	
	SS	BA	FGDG	PG	500 °C	900 °C
TA	1	0.3	0.3	-	TA-500	TA-900
TB	1	0.3	0.15	0.15	TB-500	TB-900
TD	1	0.3	-	0.3	TD-500	TD-900

4.2.1 Pyrolysis

Figure. 9 presented a schematic diagram of an experimental system for pyrolysis able to operate at temperatures up to 1200°C. The pyrolysis process was conducted using electric laboratory tube furnace Carbolite® Typ 301 (Carbolite Gero; UK), the system used a horizontal quartz tube along with a nitrogen cylinder and volatiles collection system.

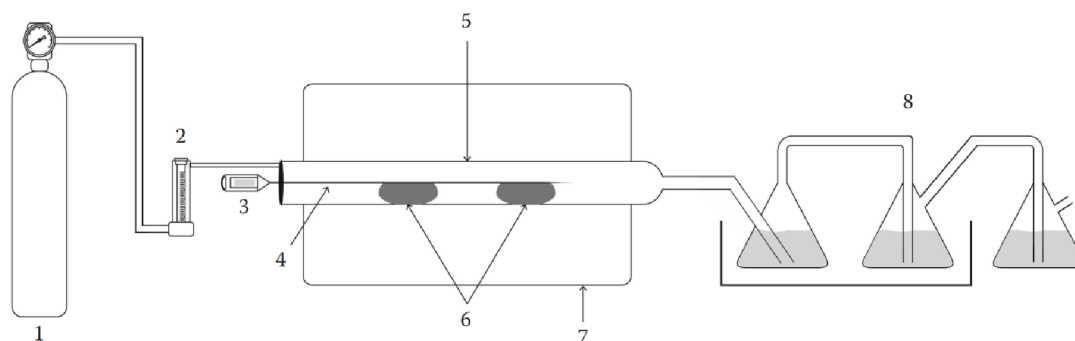


Figure 9. Schematic diagram of laboratory pyrolysis apparatus. 1) Nitrogen source, 2) Gas flow meter, 3) Thermometer, 4) Thermometer probe, 5) Quartz tube, 6) Ceramic sample holders, 7) electric furnace, 8) Volatiles collecting system (Mercl et al., 2020)

Well mixture samples (TA, TB, TD, SS, FGDG, PG, and BA) weight of 3g (particle size <1mm) were pyrolyzed. The furnace was preheated, and once the desired temperature reached (500°C and 900°C) The samples placed in ceramic crucibles, were introduced into a quartz tube with 4.5 cm internal diameter and 95 cm length with total volume of 0.6711 L. The samples were kept in the operating furnace for 30 minutes, under a stream of N₂ (99.999%) at rate of 100 L/h. The volatiles were absorbed on three conical flasks filled as follows: the first two flasks filled with Chloroform (CHCl₃) and the last one filled with nitric acid (HNO₃). These flasks were kept in the ice bath to collect condensable vapors of the vented gases. After pyrolysis the samples were then removed from the furnace, air dry, weighted and stored in airtight plastic container.

4.2.2 pH content

The value of the pH of the samples was determined following extraction with 0.01 mol/L CaCl₂ in a 1:5 ratio. After shaking for 2 hours at 180 rpm at room temperature, the supernatant of the solution was measured using a calibrated pH meter probe (Mercl et al., 2020).

4.2.3 Total content of elements

Microwave Digestion of feedstock materials

Microwave digestion of 0.3g of SS, BA, FGDG, PG, and biochar production using PTFE vessels, the addition of 10 ml of HCl (SS and BA sample), and 10ml of HNO₃ (FGDG and PG sample) into vessels and insertion into the rotor and started the digestion for 1 h by using Ethos 1 (MLS GmbH, Germany). The liquid then went through the microwave system for acid evaporation. The remaining liquid was diluted with demi water to reach a volume of 25 ml before being subjected to analysis through ICP-OES.

Dry decomposition of biochar samples

The total contents of elements in biochar sample were determined by inductive coupled plasma optical emission spectrometry (ICP-OES; Agilent 720, Agilent Technologies Inc., Santa Clara, USA) after the dry-ashing by consecution burning at different time and temperatures.

The dry sample is insert on the heating plate, stating with the plate temperature of 160 °C, after one hour the temperature was increased to 220°C, followed by one hour the temperature was raised to 280 °C and after one hour to 350 °C for another one hour and the samples were moved to the oven and the process go overnight (14 hours).

The HNO₃ was added to the samples and transferred to PTFE cups using the ultrasonic bath, then placed on the heating plate under the fume hood at 130°C during 1 hour of evaporation. Following to the oven at a temperature of 500°C for 1 hour. After cooling down HNO₃ and HF 2:1 v/v ratio, was added to the sample (10ml of HNO₃ and HF) and boiled to dryness at 160 °C for 4 hours. Subsequently, for 10 minutes at 120°C, a dilution is made with 3 ml aqua-regia solution: HNO₃: HCL, 3:1 v/v. Following this procedure, demineralized water is added to the solution to reach a final volume of 25ml, and then determined by ICP-OES (Mercl et al., 2020).

4.2.4 Bioavailable fraction of elements

The bioavailability of potential toxic elements (As, Cd, Cr, Pb), macronutrients (Ca, K, Mg, P, S), micronutrients (Cu, Fe, Mn, Ni, Zn) in biochar samples were determined by diluted acetic acid extraction of 0.3g of sample mixed with 0.11M CH₃COOH. For SS and BA at the ratio of 1:100 w/v, and for FGDG and PG, the ratio of 1:40 w/v. The samples were shaken at 120 rpm for 16 h at room temperature. This step was followed by centrifugation of the supernatant samples at 6800 rpm (9400g) for 10 minutes. The content of the elements was determined in the supernatant using an inductively coupled plasma optical emission spectrometer, ICP-OES.

4.2.5 Element analysis

The total elemental composition of Carbon (C), Hydrogen (H), Nitrogen (N), and Sulfur (S) in the material (SS, BA, FGDG, PG) was analyzed through an elemental analyzer (CHNS Vario MACRO cube, Elementar Analysensysteme, Hanau, Germany) (Mercl et al., 2020).

The organic elemental analysis involves the high-temperature oxidation/digestion of elements (C, H, N, S) into gaseous oxidation products (CO₂, H₂O, NO_x, and SO₂). Once the gas has been treated and separated, quantitative measurements are performed using a suitable detector (TCD, IR, etc.).

4.2.6 Statistical and data analysis

The statistical analysis was conducted to assess the content of the element in total and available contents (macronutrients, micronutrient, and potential toxic element) from pyrolyzed materials and co-pyrolyzed mixture at both temperatures. The relative availability of nutrients was

calculated by dividing the available content in the biochar by its total content in the of nutrients and expressing in percentage.

In the case of this study, statistical analysis was performed using two-way ANOVA model with each element as a dependent variable and temperature, mixture of the sample as a factor variable. For the mixture and raw material was followed by post-hoc Tukey Honest Significant test, but this test was not applicable to the temperature. The result was presented graphically throughout the comparison of the elements. The significant level of 0.05 (P value) for all case of analyses. The statistical analysis was carried out using IBM SPSS Analysis 25.

5 Results

5.1 Characterization of feedstock materials and mixtures

Sewage sludge (SS), biomass ash (BA), flue gas desulfurization gypsum (FGDG), and phosphogypsum (PG) were analysed in terms of the total and available content of seventeen elements, which were congregated in four different groups: potential toxic elements (As, Cd, Cr, Pb), macronutrients (Ca, K, Mg, P, S), micronutrients (Cu, Fe, Mn, Mo, Ni, Zn).

In Table 7, the initial content of potentially toxic elements shows some differences between the feedstocks studied. The table indicates that FGDG has the most significant level of As (111.33 ± 9.38 mg/kg), exceeding the content of Cd in BA by more than 16 times. As and Cd content were below limit of detection (As <2.5 mg/kg, Cd <0.08 mg/kg) in PG. Table 8 reveals distinct macronutrient, FGDG has the highest contents of S (132.95 ± 12.99 mg/kg) and Ca (213.94 ± 21.88 mg/kg), BA containing more than 90 times of K compared to other materials. Micronutrients in table 8, Cu, Fe, Zn were higher in SS (Cu and Zn is 74 times and 95 times higher than FGDG).

Table 7. Initial potential toxic elements content (mg/kg) of feedstock materials

	Potentially toxic elements			
	As mg/kg	Cd mg/kg	Cr mg/kg	Pb mg/kg
SS	5.36 ± 0.51	0.83 ± 0.19	28.81 ± 9.17	22.55 ± 11.72
BA	8.09 ± 0.28	3.26 ± 0.06	5.47 ± 0.14	18.38 ± 0.68
FGDG	111.33 ± 9.38	0.19 ± 0.03	3.03 ± 0.24	2.88 ± 0.86
PG	BDL	BDL	0.3 ± 0.05	9.05 ± 0.54

BDL : Below detection limit for As < 2.5 , Cd <0.08 mg/kg

Table 8. Initial macronutrient content (g/kg) of feedstock material

	Macronutrients				
	Ca g/kg	K g/kg	Mg g/kg	P g/kg	S g/kg
SS	31.77 ± 4.93	3.23 ± 0.78	4.68 ± 0.76	28.13 ± 14.02	10.03 ± 2.43
BA	18.26 ± 0.14	247.41 ± 1.23	4.25 ± 0.05	13.64 ± 0.27	43.95 ± 0.43
FGDG	213.94 ± 21.88	1.07 ± 0.44	2.26 ± 0.19	0.77 ± 0.27	132.95 ± 12.99
PG	175.54 ± 21.05	0.26 ± 0.03	0.03 ± 0.02	1.29 ± 0.07	112.15 ± 13.36

Table 9. Initial micronutrient content (mg/kg) of feedstock materials

	Micronutrient				
	Cu mg/kg	Fe mg/kg	Mn mg/kg	Ni mg/kg	Zn mg/kg
SS	2.14 ± 38	53395 ± 29838	378 ± 80.16	22.68 ± 0.58	955 ± 200
BA	25.92 ± 0.82	2841 ± 393	410 ± 0.76	3.56 ± 0.49	527 ± 9.12
FGDG	2.81 ± 0.50	900 ± 61.97	94.46 ± 7.42	1.79 ± 0.26	12.08 ± 3.7
PG	18.68 ± 2.48	281 ± 31.51	2.25 ± 0.59	0.58 ± 0.61	9 ± 1.75

In the case of feedstocks, available content of potentially toxic elements is shown in table 10. For As, the highest average contents in FGDG (57.11 ± 1.92 mg/kg), but SS is below limit of detection level (As < 3 mg/kg). Also, for Pb, in each feedstocks shown that the content of Pb is all below detected level (Pb < 0.8 mg/kg). However, Cd and Cr has the highest average content in BA with 3.16 ± 0.09 mg/kg and 1.55 ± 0.03 mg/kg.

Table 10. Feedstock materials–Available Toxic elements content (mg/kg)

	Potentially toxic elements			
	As mg/kg	Cd mg/kg	Cr mg/kg	Pb mg/kg
SS	BDL	0.36 ± 0.06	BDL	BDL
BA	12.66 ± 0.51	3.16 ± 0.09	1.55 ± 0.03	BDL
FGDG	57.11 ± 1.92	0.11 ± 0.02	0.21 ± 0.004	BDL
PG	3.31 ± 0.29	BDL	BDL	BDL

BDL: Below detection limit for As < 3, Cr < 0.5, Pb < 2 mg/kg for SS and BA and Cd < 0.04 and Pb < 0.8 mg/kg for FGDG and PG.

In table 11 shown the content of feedstock macronutrients in g/kg, Ca with the highest content (37.14 ± 0.56 g/kg) has found in SS. BA was found to have the highest content in K with 267.19 ± 11.82 g/kg compared to other feedstocks, for S with 63.29 ± 3.90 g/kg and P with 13.74 ± 0.69 g/kg. For K content in SS is very low with 1.10 ± 0.03 g/kg.

Table 11. Feedstock materials–Available Macronutrients content (g/kg)

	Macronutrients				
	Ca g/kg	K g/kg	Mg g/kg	P g/kg	S g/kg
SS	37.14 ± 0.56	1.10 ± 0.03	4.57 ± 0.06	8.65 ± 0.05	8.90 ± 0.18
BA	20.23 ± 0.98	267.19 ± 11.82	5.9 ± 0.39	13.74 ± 0.69	63.29 ± 3.90
FGDG	26.57 ± 0.32	0.09 ± 0.01	0.81 ± 0.01	0.001 ± 0.01	20.72 ± 0.39
PG	26.29 ± 0.03	0.05 ± 0.02	0.0004 ± 0.001	0.10 ± 0.026	20.82 ± 0.092

In the case of micronutrients of feedstock are shown in table 12, the highest content of Fe at 2087.42 ± 78.10 mg/kg, ash had the highest Mn at 356.48 ± 22.09 mg/kg, for FGDG, PG and SS displayed the lowest content of Mo which is below limit of detection ($\text{Mo} < 0.5$ mg/kg) and at the highest content in Cu is found in SS with 12.96 ± 0.19 mg/kg, followed by Zn with 729.36 ± 6.56 mg/kg.

Table 12. Feedstock materials–Available Micronutrients content (mg/kg)

	Micronutrient					
	Cu mg/kg	Fe mg/kg	Mn mg/kg	Mo mg/kg	Ni mg/kg	Zn mg/kg
SS	12.96 ± 0.19	2087.42 ± 78.10	272.80 ± 1.23	BDL	9.73 ± 0.28	729.36 ± 6.56
BA	BDL	23.05 ± 1.29	356.48 ± 22.09	2.78 ± 0.12	1.96 ± 0.17	561.03 ± 21.50
FGDG	1.15 ± 0.07	70.17 ± 2.88	92.27 ± 1.65	BDL	0.75 ± 0.01	3.55 ± 0.41
PG	1.13 ± 0.13	18.57 ± 0.48	BDL	BDL	BDL	0.25 ± 0.11

BDL: Below detection limit for Cu < 0.5 , Mn < 0.04 , Ni < 0.2 and Mo < 0.5 mg/kg

In table 13 shows the pH content of the pyrolyzed feedstock and mixture samples. Biochar of feedstock and mixture has pH range between 6 to 10. After pyrolysis, all the samples (feedstocks and mixture) have increased in pH value when temperature rises. For mixture sample, TA TB and TD has a similar increased of pH value from 9 at 500°C to 12 at 900°C.

Table 13. pH value for pyrolyzed feedstock and mixture

Pyrolyzed feedstock	Temp	pH
SS	500	7.83 ± 0.007
	900	10.5 ± 0.014
BA	500	11.08 ± 0.007
	900	12.70 ± 0.007
FGDG	500	7.51 ± 0.078
	900	8.28 ± 0.064
PG	500	6 ± 0.156
	900	6.32 ± 0.014
TA	500	9.42 ± 0.004
	900	12.01 ± 0.277
TB	500	9.44 ± 0.047
	900	11.96 ± 0.216
TD	500	9.38 ± 0.294
	900	11.89 ± 0.088

Table 14 presented the percentage composition of C, N, H and S in each sample (feedstocks and pyrolytic mixture). For feedstocks, SS has the highest content of N, C, H was found to be $4.53 \pm 0.05 \%$, $27.32 \pm 0.25\%$ and $4.76 \pm 0.44\%$ respectively compared to the other sample. Among the pyrolytic mixture samples, shown a similar content of C, N, H and S.

Table 14. Initial CHNS ratio (%) of the feedstocks

	Elements			
	N [%]	C [%]	H [%]	S [%]
SS	4.53 ± 0.05	27.32 ± 0.25	4.76 ± 0.44	
				1.32 ± 0
BA	0.23 ± 0.02	17.62 ± 0.25	0.30 ± 0.09	
				4.27 ± 0
FGDG	0.01 ± 0.01	0.07 ± 0.01	0.73 ± 0.04	
				6.34 ± 0.88
PG	0.004 ± 0.01	0.03 ± 0.01	2.43 ± 0.07	
				7.89 ± 0.13
TA	0.84 ± 0.71	11.98 ± 3.38	0.27 ± 0.13	
				8.82 ± 2.33
TB	0.83 ± 0.74	12.14 ± 4.41	0.30 ± 0.14	
				8.40 ± 1.94
TD	0.87 ± 0.73	12.92 ± 3.09	0.30 ± 0.14	
				8.15 ± 2.06

5.2 Biochar yield

Co-pyrolysis biochar was weighted and calculated and presented in percentage by comparing all the mixtures and temperatures. In Figure 10 illustrates the yield in mixtures TA, TB, and TD at temperature of 500°C and 900°C, with all mixture has decreasing trend of biochar yield when increasing the temperature. For TA yield of biochar decreased from 71% at 500°C, to 47% at 900°C, for TB from 70% at 500°C, to 46% at 900°C, while TD exhibits the lowest yield decreased from 69% at 500°C, to 45% at 900°C.

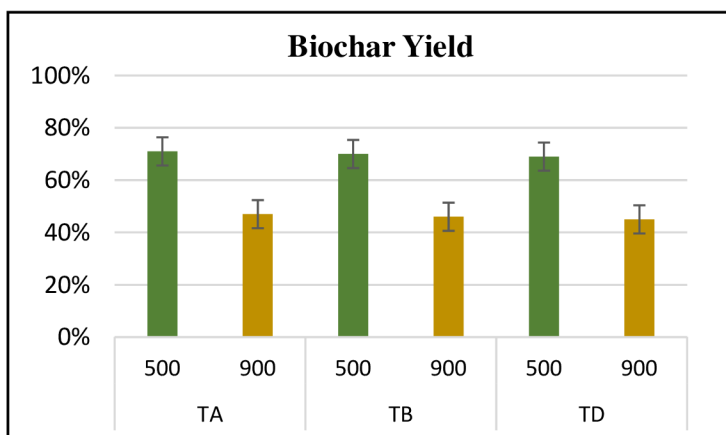


Figure 10. Biochar yield of pyrolyzed feedstock (%)

5.3 Total Content of elements in pyrolyzed materials

The effect of co-pyrolysis mixture and temperature is shown in the following table. The table 15 presents the contents of potentially toxic elements in pyrolyzed materials at different temperatures (500°C and 900°C), measured in milligrams per kilogram (mg/kg). The highest content of As is observed in the FGDG consistently at both temperatures compared to the initial content, while the lowest is below limit of detection (As < 2.5 mg/kg) in PG at 500°C. At 900°C, Cd increased in PG (54.24 ± 60.3 mg/kg, 50 times higher compared to the initial value). Additionally, SS displays increase in Cr at 900°C (85.17 ± 2.24 mg/kg). In the case of, Cr has the highest content ranging from TD at 900°C with 64.5 ± 5.08 mg/kg to 62.7 ± 2.13 mg/kg with TB at 900°C, while the lowest content was found in TB at 500°C with 42.8 ± 0.34 mg/kg. This was followed by the highest content of As, TA at 500°C with 26.7 ± 1.31 mg/kg and the lowest at TD 500°C with 19.5 ± 0.72 mg/kg. For Pb had the highest average content in TA at 500°C with 22.1 ± 0.76 mg/kg while the lowest at TA 900°C with 13.8 ± 2.09 mg/kg. However, Cd has the lowest content compared to other elements with the lowest content at TB at 900°C (0.46 ± 0.10 mg/kg) and the highest with 1.5 ± 0.06 mg/kg at TA at 900°C.

Table 15. Pyrolyzed material total content – Potential toxic elements (mg/kg)

Potentially Toxic Elements					
	Temp	As mg/kg	Cd mg/kg	Cr mg/kg	Pb mg/kg
SS	500	7.21 ± 0.25	1.12 ± 0.11	78.3 ± 0.89	44.17 ± 0.23
	900	6.28 ± 0.55	0.16 ± 0.03	85.17 ± 2.24	4.82 ± 1.52
BA	500	8.81 ± 0.33	1.91 ± 0.06	6.15 ± 0.28	18.04 ± 0.08
	900	13.18 ± 0.9	BDL	9.71 ± 1.18	9.78 ± 0.42
FGDG	500	114.88 ± 5.89	2.4 ± 0.41	3.75 ± 0.47	3.45 ± 0.61
	900	108 ± 4.96	1.61 ± 0.25	4.21 ± 0.23	1.65 ± 0.2
PG	500	BDL	21.57 ± 1.23	0.59 ± 0.06	9.71 ± 0.05
	900	5.47 ± 3.61	54.24 ± 60.3	22.11 ± 36.41	47.9 ± 67.01
TA	500	26.7 ± 1.31	1.5 ± 0.06	54.55 ± 0.31	22.1 ± 0.76
	900	26.65 ± 4.12	0.59 ± 0.005	63.76 ± 5.17	13.8 ± 2.09
TB	500	22.2 ± 1.24	1.45 ± 0.08	42.8 ± 0.34	21.9 ± 2.68
	900	24.8 ± 2.45	0.46 ± 0.10	62.7 ± 2.13	15.95 ± 0.84
TD	500	19.5 ± 0.72	1.42 ± 0.07	45.36 ± 1.73	23.1 ± 0.38
	900	24.6 ± 1.42	0.5 ± 0.01	64.5 ± 5.08	16.5 ± 1.83

BDL : Below detection limit for Cd<0.08, As < 2.5 mg/kg

Table 16 provides insights into the macronutrients total content of feedstock's biochar at both temperatures. Notably, FGDG at 500°C exhibits the highest Ca content (285.25 ± 8.85 mg/kg) and S content decreases at 500°C (192.24 ± 9.51 g/kg) but shows an increase at 900°C (178.14 ± 1.50 g/kg). Reported P contents increased from initial level in SS was 28.13 ± 14.02 g/kg to 64.49 ± 0.36 g/kg at 500°C. For K decreased from 247.41 ± 1.23 g/kg in raw biomass ash to 207.66 ± 21.54 g/kg at 900°C of biomass ash. The initial content of K in feedstock was found

to be high in biomass ash (247.41 g/kg), which is more than 70 times more than the amount of K in SS. Following the pyrolysis, K in SS rose to 11.09 g/kg at 900°C, while K in BA was reported to have reduced to 182 g/kg at 500°C and 207 g/kg at 900°C for BA. In the case of macronutrients, Ca was found to have the highest content in TB at 900°C (162.2 ± 2.34 g/kg), while TD at 500°C showed the lowest (103.5 ± 1 g/kg). Ca was detected to have a higher content when increasing the temperature to 900°C. In the case of potential toxic elements in co-pyrolytic mixture, K peaks in TB and TD at 900°C with 84.74 ± 4.65 g/kg and 84.75 ± 2.81 g/kg, the content of K has similarity among all conditions. Mg has the lowest content compared to the other element, with the highest mean content is TB at 900°C (10.73 ± 0.18 g/kg) and the lowest content in TA at 500°C (8.19 ± 0.05 g/kg). For P, the highest content in TB at 900°C (54.98 ± 0.96 g/kg) and the lowest in TA at 500°C (37.25 ± 0.7 g/kg). The content of S is shown to be increased at 900°C in each mixture, with the highest average content in TA at 900°C (95.46 ± 2.08 g/kg) and the lowest in TD at 500°C (61.22 ± 0.59 g/kg).

Table 16. Pyrolyzed feedstocks total content – Macronutrients (g/kg)

		Macronutrients				
	Temp	Ca g/kg	K g/kg	Mg g/kg	P g/kg	S g/kg
SS	500	67.34 ± 0.81	10.09 ± 0.54	11.41 ± 0.02	64.49 ± 0.36	11.18 ± 0.3
	900	41.33 ± 1.11	11.99 ± 0.01	12.32 ± 0.33	73.47 ± 2.51	11.36 ± 0.25
BA	500	11.83 ± 0.69	182.19 ± 3.09	5.67 ± 0.24	13.78 ± 0.006	44.75 ± 1.61
	900	16.7 ± 0.58	207.66 ± 21.54	8.29 ± 0.27	18.49 ± 0.36	62.61 ± 0.85
FGDG	500	285.25 ± 8.85	0.62 ± 0.02	1.55 ± 0.11	0.57 ± 0.0004	192.24 ± 9.51
	900	262.92 ± 2.26	1.31 ± 0.03	1.53 ± 0.02	0.55 ± 0.007	178.14 ± 1.50
PG	500	226.84 ± 51.97	0.33 ± 0.04	0.02 ± 0.007	1.85 ± 0.17	159.98 ± 41.37
	900	181.18 ± 77.94	1.82 ± 2.48	1.008 ± 1.70	4.20 ± 3.96	111.92 ± 88.24
TA	500	113.08 ± 4.05	80.27 ± 0.37	8.19 ± 0.05	37.26 ± 0.7	63.95 ± 3.35
	900	172.20 ± 3.56	82.78 ± 0.39	11.52 ± 0.36	54.71 ± 0.19	95.46 ± 2.08
TB	500	110.47 ± 0.75	78.01 ± 1.38	7.75 ± 0.13	37.03 ± 0.68	63.44 ± 0.11
	900	162.27 ± 2.34	84.74 ± 4.65	10.74 ± 0.18	54.99 ± 0.96	91.75 ± 1.19
TD	500	103.55 ± 1	79.56 ± 1.01	7.42 ± 0.04	37.81 ± 0.51	61.22 ± 0.59
	900	159.32 ± 2.09	84.76 ± 2.81	10.73 ± 0.5	56.33 ± 0.74	89.45 ± 0

Table 17 provides insight into the micronutrients of pyrolyzed feedstocks. Notable increased with temperature increase of Cu and Mn content in SS at 900°C (510 ± 17.38 mg/kg and 790 ± 24.4 mg/kg), while FGDG had the lowest content of Cu at 900°C (1.61 ± 0.25 mg/kg) in results obtained for Mn in PG at 500°C (1.25 ± 0.27 mg/kg). In addition, SS was presented the highest content of Fe at 900 (133729 ± 4565 mg/kg), while the rest of pyrolyzed waste material exhibited the increased content of Fe when increase the temperature. However, Ni content had slightly increased with temperature increase in SS at 900°C (53.9 ± 2.84 mg/kg). In the case of Zn, the content significantly dropped from 5556 ± 12.55 mg/kg at 500 to 712 ± 7.35 mg/kg in BA.

Micronutrient of the pyrolytic mixture after pyrolysis, Fe has the highest average content compared to the other elements, the highest content of Fe is in TD at 900°C (80016 ± 2487 mg/kg) and the lowest in TA at 500°C (57564 ± 778 mg/kg) and TB at 500°C (57200 ± 1475 mg/kg). For Cu, the average content is observed to increase at 900°C, the highest content in TD at 900°C (352 ± 8.06 mg/kg). Regarding Zn, the high content is in TB at 500°C (1131 ± 31.47 mg/kg) and TD at 500°C (1141 ± 18.64 mg/kg), Mn has increased slightly when increasing temperature to 900°C, the highest average is in TA at 900°C (699 ± 14.9 mg/kg) and the lowest is in TD at 500°C (459 ± 1.75 mg/kg). For Ni was found to be the lowest content among the other element, the lowest average content of Ni is in TB at 500°C (29.15 ± 0.08 mg/kg) and the highest content reached to 41.97 ± 1.31 mg/kg in TB at 900°C.

Table 17 Pyrolyzed feedstocks total content – Micronutrients (mg/kg)

		Micronutrients				
	Temp	Cu mg/kg	Fe mg/kg	Zn mg/kg	Mn mg/kg	Ni mg/kg
SS	500	430.35 ± 4.67	112564 ± 553	1799 ± 5.05	659 ± 11.52	50.76 ± 2
	900	510 ± 17.38	133729 ± 4565	223 ± 3.70	790 ± 24.4	53.9 ± 2.84
BA	500	35.78 ± 1.32	2986 ± 584	5556 ± 12.55	392 ± 6.01	4.16 ± 0.18
	900	46.25 ± 0.9	5202 ± 2584	712 ± 7.35	567 ± 8.18	6.21 ± 0.2
FGDG	500	2.4 ± 0.41	1223 ± 57.21	7.73 ± 1.81	95.72 ± 0.04	1.86 ± 0.39
	900	1.61 ± 0.25	1448 ± 45.52	2.56 ± 0.6	89.04 ± 1.62	2.29 ± 0.11
PG	500	21.57 ± 1.23	418 ± 51.56	8.14 ± 1.9	1.25 ± 0.27	0.55 ± 0.004
	900	54.24 ± 60.34	59.47 ± 95.41	443 ± 755	117 ± 197	10.23 ± 16.17
TA	500	230 ± 5.02	57564 ± 778	1132 ± 24.03	483 ± 2.41	34.84 ± 0.3
	900	337 ± 0.79	77471 ± 1099	1075 ± 93.91	699 ± 14.9	41.86 ± 1.86
TB	500	227 ± 2.2	57200 ± 1475	1131 ± 31.47	468 ± 7.73	29.15 ± 0.08
	900	340 ± 1.81	76900 ± 1564	1040 ± 105	676 ± 7.52	41.97 ± 1.31
TD	500	232 ± 1.71	57465 ± 750	1141 ± 18.64	459 ± 1.75	30.72 ± 0.85
	900	352 ± 8.06	80016 ± 2487	861 ± 38.7	681 ± 14.44	41.73 ± 2.25

5.4 Available contents in pyrolyzed materials

In the case of feedstocks biochar, available potential toxic elements content is shown in table 18. For As, the highest content was found in FGDG at 500°C (105 ± 0.37 mg/kg), while the lowest was remain in SS which is below limit of detection. For Cd contents peaked in Ash at 500°C (1.79 ± 0.02 mg/kg) and registered as below limit of detection in all feedstocks at 900°C. For Cr exhibited its highest content in SS at 900°C (3.97 ± 3.3 mg/kg) and frequently fell below detection limit with PG at both temperatures. Pb value rose in content from below limit of detection in initial feedstocks to 2.97 ± 0.27 mg/kg with PG at 900°C and Ash at 500°C (2.8 ± 0.65 mg/kg), but remain below limit of detection in FGDG and SS.

Potential toxic elements in the co-pyrolytic mixture had the highest content of As compared to other elements with 13.50 ± 3.09 mg/kg in TA at 500°C and below limits detection at 900°C across all mixture. Cd and Cr also have the highest content with 0.45 ± 0.0007 mg/kg and 0.53 ± 0.01 mg/kg in TA at 500°C, and in TB reported below detected value at 900°C for As < 2.5 mg/kg, Cd < 0.08 mg/kg, Cr < 0.42 mg/kg. while Pb has the highest with 3.20 ± 0.1 mg/kg TB at 900°C. For the potential toxic elements shown the decreased in amount of the element when increasing the temperature to 900°C.

Table 18. Pyrolyzed material available content – Potential toxic elements (mg/kg)

Potentially toxic elements					
	Temp	As mg/kg	Cd mg/kg	Cr mg/kg	Pb mg/kg
SS	500	BDL	0.21 ± 0.03	BDL	BDL
	900	BDL	BDL	3.97 ± 3.3	BDL
BA	500	7.84 ± 0.1	1.79 ± 0.02	1.61 ± 0.13	2.8 ± 0.65
	900	BDL	BDL	1.37 ± 0.05	BDL
FGDG	500	105 ± 0.37	0.1 ± 0.01	0.7 ± 0.006	BDL
	900	85.88 ± 0.71	BDL	BDL	BDL
PG	500	BDL	BDL	BDL	1.06 ± 0.13
	900	1.47 ± 0.46	BDL	BDL	2.97 ± 0.27
TA	500	13.5 ± 3.094	0.45 ± 0.00077	0.53 ± 0.015	2.73 ± 0.46
	900	BDL	0.055 ± 0.077	BDL	2.62 ± 0.26
TB	500	10.64 ± 0.52	$0.27 \pm .0386$	0.241 ± 0.341	1.26 ± 1.78
	900	BDL	BDL	BDL	3.2 ± 0.104
TD	500	BDL	0.36 ± 0.109	0.238 ± 0.336	1.11 ± 1.58
	900	BDL	0.1 ± 0.006	BDL	2.8 ± 0.15

BDL: Below detection limit for As <3, Cd < 0.1, Cr < 0.5, Pb < 2 mg/kg for SS and Ash and As <1.2, Cd < 0.04, Cr < 0.2, Pb < 0.8 mg/kg for FGDG and PG. As < 2.5, Cd < 0.08, Cr < 0.42 mg/kg for TA, TB, and TD

The following figure contains the available content in percentage for evaluated samples. In figure 11, it is possible to notice the relative availability of toxic elements for TA. For As and Cr reported at maximum availability at 500°C (50% and 1%) and below limits detection at 900°C, for Cd the relative availability has decrease with temperature 30% at 500°C and 9% at 900°C. On the other hand, Pb has increased in temperature 12% at 500°C to 19% at 900°C.

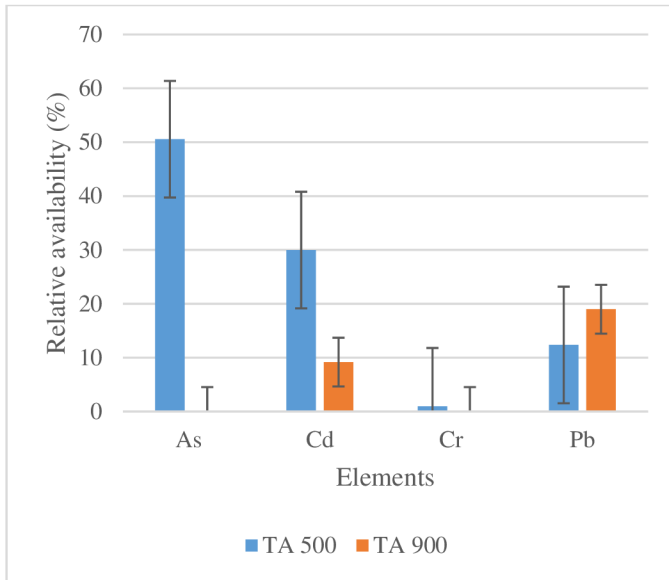


Figure 11. Relative availability content of potential toxic element in TA (%)

In figure 12, the relative availability in TB such as As, Cd and Cr were higher at 500°C (47%, 18%, 0.5%) and below limits detection for 900°C, very similar trend compared to TA, Pb portions was very low 6% at 500°C and increased to 20% at 900°C.

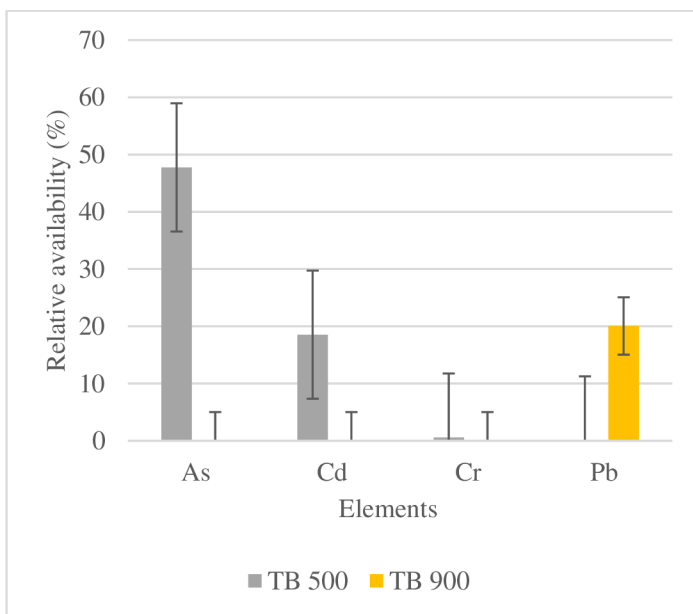


Figure 12. Relative availability content of potential toxic element in TB (%)

In figure 13, TD relative availability of Cd has the highest portion decreasing in temperature from 25% at 500°C to 20% at 900°C. In the case of Pb has increased with from 5% at 500°C to 17% at 900°C. For Cr has a very low portion at 500°C (0.5%) and decreased at 900°C to below limit of detection for Cr. TD was reported to have the lowest As which is below limit of detection, while higher relative availability in Cd and Pb compared to TA and TB.

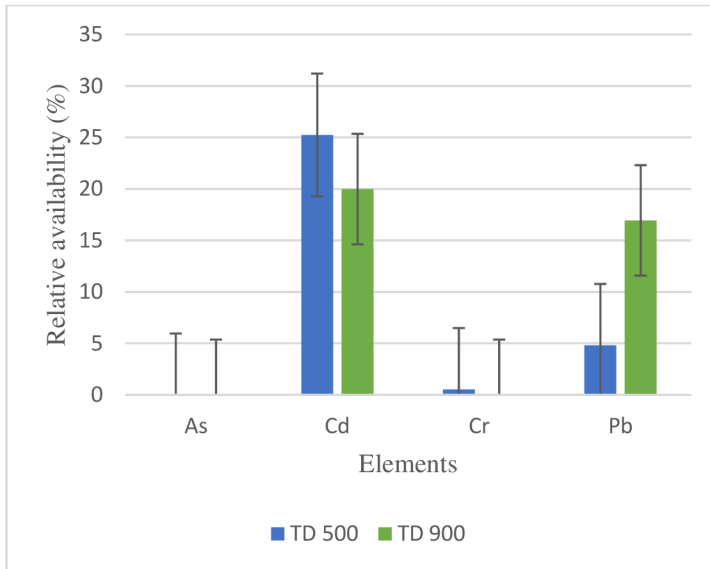


Figure 13. Relative availability content of potential toxic element in TD (%)

Table 19 presents the available content of feedstock biochar macronutrients, for SS feedstock at 900°C has the highest contents of Ca with (80.46 ± 62.89 g/kg) and its lowest at 500°C (17.18 ± 0.12 g/kg). K content in biomass ash rose at 900°C (343.59 ± 20.04 g/kg). For Mg has the lowest content in PG at 900°C (0.001 ± 0.0004 g/kg) and high in SS with 13.8 ± 10.74 g/kg at 900°C. Meanwhile P has the highest content with SS at 500°C (16.82 ± 15.153 g/kg) and highest content of S at 500°C (51.376 ± 0.63 g/kg) in biomass ash. The content of Ca, K and S in SS and BA increased with higher temperature, while P reported to have reduced the content at 900°C.

In addition, co-pyrolysis macronutrients available content such as Ca, Mg and S were increasing with increase temperature. Ca, the highest content is observed in TA at 900°C with 125.67 ± 7.33 g/kg, while the lowest is in TD at 500°C with 82.77 ± 0.413 g/kg. TA at 500°C exhibits the highest content of K with 70.53 ± 0.58 g/kg and the lowest with 47.75 ± 0.88 g/kg in TD at 900°C. However, K content was decreased with temperature 900°C. For P, the highest content is observed with 4.917 ± 0.09 g/kg in TA at 500°C and the lowest is 3.027 ± 0.303 g/kg in TD at 500°C. However, S has the greatest content with 91.224 ± 78.04 g/kg and Mg with 6.121 ± 0.131 g/kg in TA at 900°C while the lowest is 3.027 ± 0.303 g/kg in TD 500°C for S and 37.25 ± 35.82 g/kg in TD at 900°C for Mg. Among all the elements, Ca, S and K show the most outstanding content.

Table 19 Pyrolyzed material available content – Macronutrients (g/kg)

Macronutrients						
	Tem P	Ca g/kg	K g/kg	Mg g/kg	P g/kg	S g/kg
SS	500	24.44 ± 2.49	0.826 ± 0.01	2.803 ± 1.86	2.09 ± 0.28	2.05 ± 0.147
	900	80.46 ± 62.89	2.422 ± 2.006	13.809 ± 10.747	16.82 ± 15.153	0.99 ± 0.812
BA	500	17.18 ± 0.12	294.72 ± 7.098	4.294 ± 0.03	13.36 ± 0.181	51.376 ± 0.63
	900	27.92 ± 1.185	343.59 ± 20.04	6.994 ± 0.28	12.99 ± 0.95	6.554 ± 0.105
FGDG	500	29.87 ± 0.42	0.24 ± 0.11	0.79 ± 0.007	0.277 ± 0.06	21.23 ± 0.265
	900	27.97 ± 0.77	0.229 ± 0.01	0.23 ± 0.001	0.24 ± 0.0001	17.74 ± 0.38
PG	500	30.76 ± 1.313	0.08 ± 0.002	0.001 ± 0.0006	0.30 ± 0.02	21.29 ± 1.153
	900	28.05 ± 1.001	0.11 ± 0.01	0.001 ± 0.0004	0.67 ± 0.07	19.06 ±1.153
TA	500	92.95 ± 0.49	70.53 ±0.58	3.572 ± 0.106	4.917 ± 0.09	64.96 ± 0.95
	900	125.67 ± 7.33	49.003 ± 0.87	6.121 ± 0.131	1.768 ± 0.28	91.22 ± 78.04
TB	500	90.48 ± 3.34	69.57 ± 0.122	3.219 ± 0.15	4.827 ± 0.21	63.12 ± 3.37
	900	112.27 ± 2.25	48.84 ± 1.84	5.715 ± 0.14	1.267 ± 0.33	82.58 ± 23.97
TD	500	82.77 ± 0.413	66.69 ± 3.09	3.027 ± 0.303	4.50 ± 0.12	56.54 ± 0.31
	900	105.22 ± 2.75	47.75 ± 0.88	5.285 ± 0.46	0.321 ± 0.29	37.25 ± 35.82

Figure 14, presents the relative availability of macronutrients in TA. For K, Ca and S shown the highest relative availability by decreasing from (88%, 82% and 102%) at 500°C to (59%, 73%, 96%) at 900°C. While P has the lowest portion decreased from 13% at 500°C to 3% at 900°C. Certain elements exhibit greater result of nutrients at 500°C and decreased when increase temperature for TA. The content of Mg has increased from 500°C (44%) to 900°C (53%).

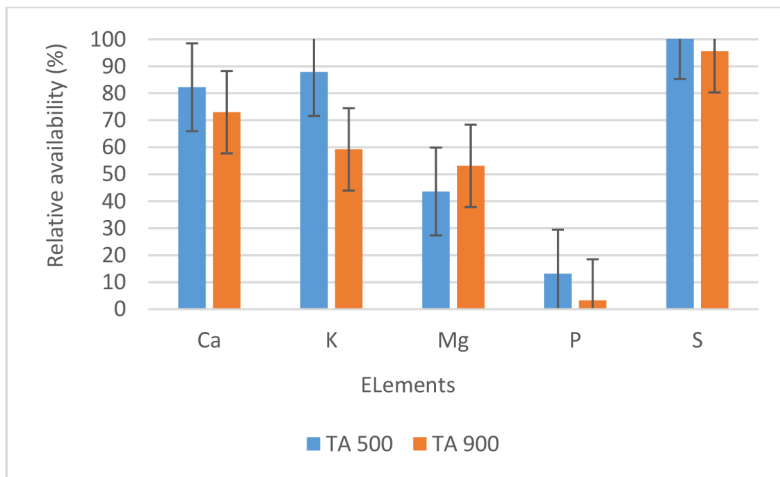


Figure 14. Relative availability content of Macronutrient in TA (%)

In the case of TB, the relative availability shows similar behaviour of the elements in TA as presented in figure 15. P still very low portion then the rest of the macronutrients at 500°C (13%) then decrease at 900°C (2%). For Mg shown the increasing of portion form 42% at 500°C to 53% at 900°C. At 500°C the relative availability of Ca, S and K were 82%, 13% and 89% higher than the portion in 900°C with 82%, 100% and 89% respectively.

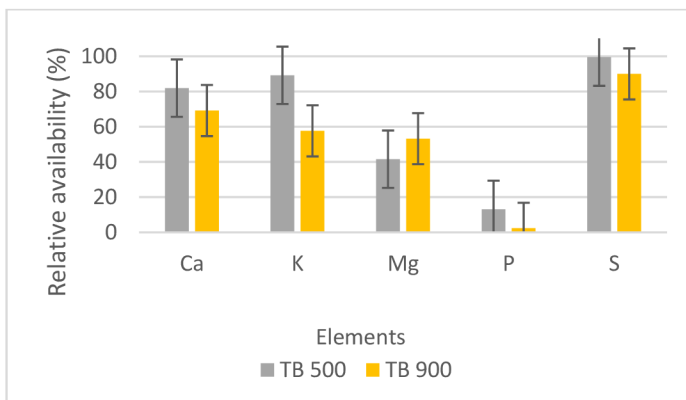


Figure 15. Relative availability content of Macronutrient in TB (%)

Figure 16, presented the relative availability in TD, for Ca, K and S were decreased by increasing in temperature from 80% at 500°C to 66% at 900°C for Ca, 84% at 500°C to 56% at 900°C for K and 92% at 500°C to 42% at 900°C. Mg goes from 41% at 500°C then increased to 49% at 900°C. However, for P the higher relative availability was 12% at 500°C and below limits detection at 900°C. The macronutrient in TD has slightly lower value of the relative availability of all the elements compared to the other mixture.

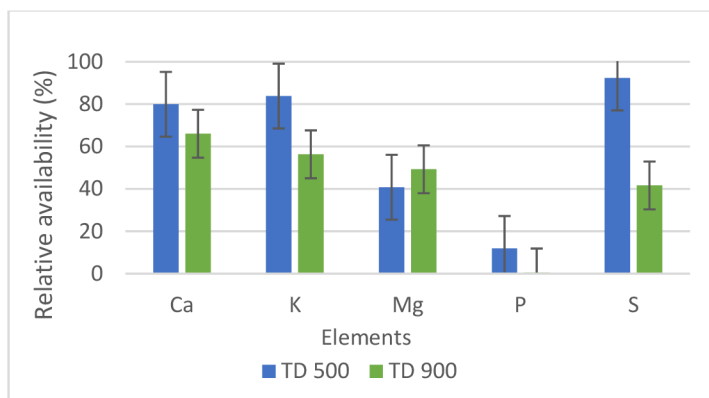


Figure 16. Relative availability content of Macronutrient in TD (%)

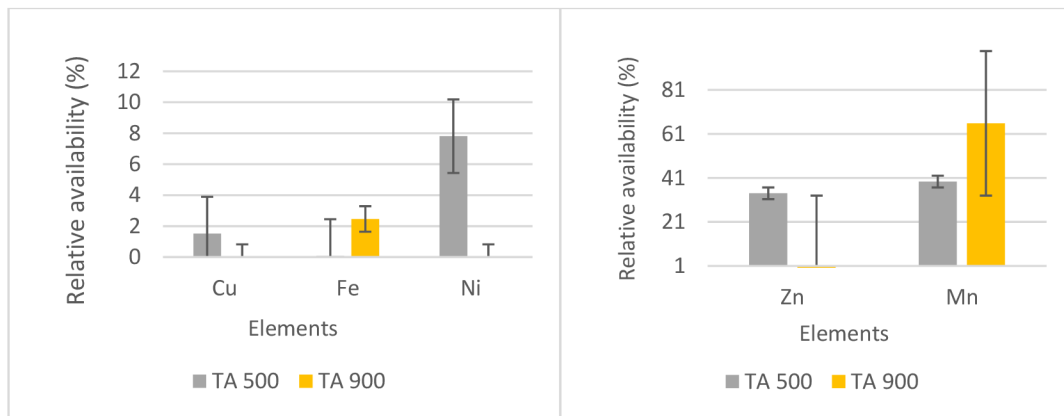
In table 20 established the feedstock biochar available micronutrient contents. The highest Cu content is observed in SS at 900°C (201 ± 134 mg/kg), while the lowest is in FGDG at 900°C (0.31 ± 0.07 mg/kg). For Fe, the maximum content found in SS at 500°C (554 ± 581 mg/kg), and the minimum content is in PG at 900°C (4.61 ± 0.02 mg/kg) which are lower than the initial value. Mn peaks in SS at 900°C (909 ± 676 mg/kg) and hits its low level in PG. For Zn is at its highest content with Ash at 500°C (527 ± 7.92 mg/kg) and lowest in FGDG at 900°C (0.44 ± 0.05 mg/kg). Also, Zn reported in SS has significant decreased to 77.5 ± 57.6 g/kg at 900°C. However, Mo remains below limit of detection for SS, FGDG and PG.

The presence of macronutrients available content in co-pyrolysis feedstocks was found with Cu at the highest value 7.37 ± 10.4 mg/kg in TD at 900°C, while the lowest which is below detected level in TA and TB at 900°C. For Fe is peaks with 1909 ± 1554 mg/kg in TA at 900°C and reaches its minimum at 27.79 ± 7.96 mg/kg in TD at 500°C, regarding to Mo is highest content is in TD at 900°C with 514 ± 93.96 mg/kg and the lowest only detected with 0.57 ± 0.001 mg/kg in TA at 900°C. For Mn reached the highest at 460.3 ± 23.12 mg/kg at TA 900°C and the lowest 0.287 ± 0.406 mg/kg at TD 900°C. Ni, and Zn have the highest content with only 2.72 ± 0.46 mg/kg and 385 ± 31.9 mg/kg with TA at 500°C.

Table 20. Pyrolyzed material available content – Micronutrients (mg/kg)

		Micronutrients				
	Temp	Cu mg/kg	Fe mg/kg	Mn mg/kg	Ni mg/kg	Zn mg/kg
SS	500	10.47 ± 4.73	554 ± 581	182 ± 14.2	mg/kg	mg/kg
	900	201 ± 134	457 ± 547	909 ± 676	1.73 ± 0.18	335 ± 9.27
BA	500	1.69 ± 0.17	43.09 ± 0.45	271 ± 1.16	13.38 ± 9.2	77.5 ± 57.6
	900	BDL	71.11 ± 16.74	431 ± 16.09	2.03 ± 0.12	527 ± 7.92
FGDG	500	1.25 ± 0.13	183 ± 1.67	65.58 ± 1.78	1.43 ± 0.05	478 ± 27.57
	900	0.31 ± 0.07	25.51 ± 0.35	6.67 ± 0.03	0.71 ± 0.02	1.25 ± 0.68
PG	500	4.53 ± 0.02	81.06 ± 3.87	0.17 ± 0.02	0.23 ± 0.05	0.44 ± 0.05
	900	4.2 ± 0.81	4.61 ± 0.02	0.49 ± 0.05	BDL	0.77 ± 0.15
TA	500	3.49 ± 0.36	42.38 ± 18.14	190 ± 4.42	BDL	1.39 ± 0.33
	900	BDL	1909 ± 1554	460.3 ± 23.12	2.72 ± 0.46	385.2 ± 31.9
TB	500	1.62 ± 0.11	44.35 ± 3.4	178.2 ± 0.84	0.28 ± 0.39	1.04 ± 0.82
	900	BDL	1321 ± 108	426.9 ± 10.28	2.08 ± 0.05	370.7 ± 7.14
TD	500	1.78 ± 0.48	27.79 ± 7.96	183 ± 4.7	BDL	0.62 ± 0.37
	900	7.37 ± 10.4	490.9 ± 506	0.287 ± 0.406	1.86 ± 0.17	348.1 ± 38.26

BDL: Below detection limit for Cu < 0.5, Mo < 0.5 mg/kg for SS and Ash and Mo < 0.2, Ni < 0.2 mg/kg for FGDG and PG

**Figure 17.** Relative availability content of Micronutrient in Co-pyrolysis biochar TA (%)

In figure 17, shown the availability of micronutrients in TA at 900°C were below detected for Cu, Ni and Zn but higher portion with 2% for Cu, 8% for Ni and 34% for Zn at 500°C. These elements have higher portion at 500°C and decreased when increased temperature to 900°C. In the case of Fe and Mn shown opposite trend by increased portion when increasing temperature from 0.07% at 500°C to 2% at 900°C for Fe, 39% at 500°C to 65% at 900°C for Mn.

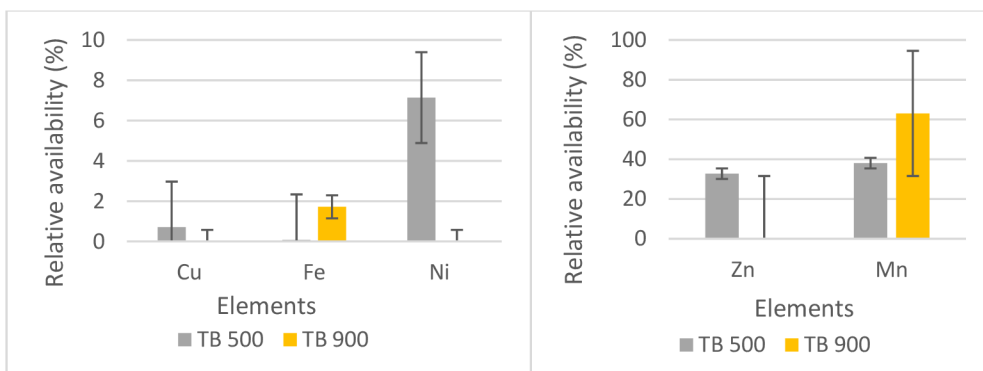


Figure 18. Relative availability content of micronutrient in co-pyrolysis biochar TB (%)

Figure 18, present the availability of micronutrient in TB which is slightly lower value of all elements compared to TA. For Cu, Ni and Zn show similarity to TA by decreased from 32% at 500°C to 0.06% at 900°C for Zn, 0.78% at 500°C for Cu, 7% at 500°C for Ni then to below limit of detection at 900°C for both elements. While Fe and Mn shown the increased relative availability in higher temperature from 0.08% at 500% to 1.7% at 900°C for Fe and from 38% at 500°C to 63% to 900°C for Mn.

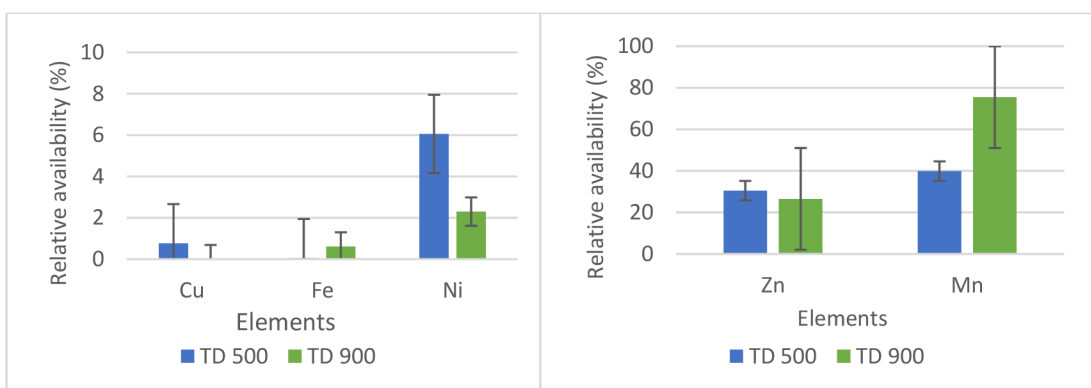


Figure 19. Relative availability content of micronutrient in co-pyrolysis biochar TD (%)

In figure 19, the relative availability content of micronutrients in TD, for Fe was found to be significantly low at temperature of 500°C (0.05%) and 900°C (0.61%). In the case of Cu, Zn and Ni shown the decreased by increasing temperature 0.77% at 500°C to below detect limit at 900°C for Cu, 30% at 500°C to 26% at 900°C for Zn and 6% at 500°C to 2% to 900°C for Ni. While Mn shown the increased with temperature from 39% at 500°C to 75% at 900°C. In the case of micronutrient, the elements repeated to be slightly lower in portion for some elements (Cu, Fe, Zn), when Zn and Mn have greater value at 900°C compared to the other mixture.

5.6 Statistical analyses

5.6.1 ANOVA and Tukey HSD test for the total content

The two-way ANOVA was performed to analyze the effect of temperature and mixture on the total content and available content of toxic elements, micronutrients, and macronutrients.

The analysis was conducted for total content of toxic elements. The result indicates that the mixture has no significant effect on toxic elements, while it was revealed that temperature had significant effect on Cd (<0.0005), Cr (<0.0005), Pb (<0.0005). For As there is no significant difference in either of these factors. The statistical significance of the elements is shown in table 21.

Table 21. ANOVA evaluation for total contents of potential toxic elements

Element	Term	<i>df</i>	<i>F</i>	<i>P. Value</i>
As	Mixture	2	4.637	.061
	Temperature	1	4.038	.091
Cd	Mixture	2	2.32	0.18
	Temperature	1	585.33	<0.0005
Cr	Mixture	2	4.18	0.07
	Temperature	1	76.96	<0.0005
Pb	Mixture	2	1.26	0.35
	Temperature	1	52.78	<0.0005

The ANOVA evaluation for macronutrient only has significant effects of temperature on K (<0.05) and P (<0.0005), but for Ca, Mg and S are statistically significant effect in temperature and mixture as shown in table 22. The pairwise comparison within mixture composition has significant difference between each mixture for Ca and Mg for S there is a significant difference between TA and TD at 900°C.

Table 22. ANOVA evaluation for total contents of macronutrients

Element	Term	<i>df</i>	<i>Meansqu</i>	<i>P. Value</i>
Ca	Mixture	2	126.169	<0.003
	Temperature	1	9263.205	<0.0005
K	Mixture	2	0.691	0.884
	Temperature	1	69.442	<0.05
Mg	Mixture	2	0.681	<0.01
	Temperature	1	30.886	<0.0005
P	Mixture	2	1.542	0.105
	Temperature	1	969.119	<0.0005
S	Mixture	2	19.113	<0.05
	Temperature	1	2584.162	<0.0005

In the case of micronutrients, temperature exhibited a statistically significant effect on Cu (<0.0005), Fe (<0.0005), Mn (<0.0005), Ni (<0.0005) and Zn (<0.05). Additionally, mixture composition has significant effects on Mn (<0.05) and Cu (<0.05) within TA and TD at 900°C indicated an interaction between the mixture composition and level of temperature has effect on the content of these elements as shown in table 23.

Table 23 ANOVA evaluation for total contents of micronutrients

Element	Term	df	F	P. Value
Cu	Mixture	2	5.614	<0.05
	Temperature	1	2267.334	<0.0005
Fe	Mixture	2	1.386	0.320
	Temperature	1	585.755	<0.0005
Mn	Mixture	2	5.503	<0.05
	Temperature	1	1490.179	<0.0005
Ni	Mixture	2	4.513	0.064
	Temperature	1	166.137	<0.0005
Zn	Mixture	2	3.059	0.121
	Temperature	1	15.694	<0.05

5.6.2 ANOVA and Tukey HSD test for available content

The analysis of variance for available contents of toxic elements shows that temperature has significant effect on Cd (<0.0005) and Cr (<0.0005), while As content is significantly influence by both mixture and temperature, the pairwise comparison revealed the significant different between TD with TA and TB at 500°C. There wasn't a statistically significant difference for Pb as shown in table 24.

Table 24. ANOVA evaluation for available contents of potential toxic elements

Element	Term	df	Meansqu	P. Value
As	Mixture	2	50.652	<0.005
	Temperature	1	194.433	<0.0005
Cd	Mixture	2	0.016	0.053
	Temperature	1	0.291	<0.0005
Cr	Mixture	2	0.029	0.506
	Temperature	1	0.344	<0.024
Pb	Mixture	2	0.525	0.618
	Temperature	1	4.13	0.089

In the case of available contents of macronutrients as shown in table 25, the ANOVA results indicate a statistically significant effects of temperature on K (<0.0005). For P, Mg, and Ca levels, the differences are observed across all conditions. The pairwise comparisons for P levels at temperature 900°C, there are significant differences between TD with TA and TD with TB.

For Mg, exhibits significant differences between TA and TD at 900°C. Ca levels show significant effect on TA with TB and TA with TD at 900°C. However, there is no significant effects are found for S, neither mixture nor temperature.

Table 25 ANOVA evaluation for available contents of macronutrients

Element	Term	df	F	P. Value
Ca	Mixture	2	18.089	<0.005
	Temperature	1	152.151	<0.0005
K	Mixture	2	2.882	0.133
	Temperature	1	503.347	<0.0005
Mg	Mixture	2	10.309	<0.05
	Temperature	1	382.988	<0.0005
P	Mixture	2	27.458	<0.005
	Temperature	1	1196.576	<0.0005
S	Mixture	2	0.841	0.476
	Temperature	1	0.175	0.690

The ANOVA results for the available content of macronutrients, indicated varied influence of temperature on the level of Fe (<0.05), Mn (<0.0005), Zn (<0.05) and Ni (<0.0005) with no significant differences in mixture. However, there was no significant difference observed in mixture or temperature for Cu as shown in table 26.

Table 26. ANOVA evaluation for available contents of micronutrients

Element	Term	df	F	P. Value
Cu	Mixture	2	0.847	0.474
	Temperature	1	0.004	0.952
Fe	Mixture	2	1.160	0.375
	Temperature	1	9.690	<0.05
Mn	Mixture	2	1.353	0.327
	Temperature	1	151.966	<0.0005
Ni	Mixture	2	2.469	0.165
	Temperature	1	100.267	<0.0005
Zn	Mixture	2	0.747	0.513
	Temperature	1	14.517	<0.05

6 Discussion

Regarding pH, the analysis samples of TA, TB and TD exhibited the pH value of 9 at 500°C, with higher pH value of 12 observed at TA 900°C, which indicates the alkalinity. with higher pH value observed at 900°C compared to 500°C, which indicates the alkalinity. This might result of the amount and composition of alkaline feedstocks SS, BA, while presence of acidic component FGDG and PG moderated the pH value. According to Chen et al. (2014), the pH level of biochar derived from municipal sewage sludge exhibited increase from 9 at a temperature of 500°C to 12 at temperature of 800°C and 900°C. This was due to the alkali salts released from the pyrolytic structure during the process. The finding of Ray et al., (2023) reported the rise in pH value in biochar with increasing the pyrolysis temperature was caused by the reduction and decomposition of acidic constituents, as well as the retention and enrichment of cations such as K and Ca in biochar.

Biochar yield in each mixture tends to decrease as the temperature rises. However, the difference between each mixture at the same temperature is shown to be very similar. The highest yield of biochar was found in TA (71% at 500°C to 47% at 900°C). Similar behaviour of biochar yield in TB with obtain value of (70% at 500°C to 46% at 900°C). Compared with TD has the lowest yield production at 500°C with only 69% and 45% at 900°C. Similar finding of the decreasing in biochar yield with raising temperature may be assigned to either secondary reaction of the solid residue, but more likely to a greater primary breakdown of the original feedstock due to additional pyrolysis conversion (Agrafioti et al., 2013). In the study of Vimal et al. (2022b), it the yield of biochar was found to be 49% and comparable to the wood biochar, with the utilisation of PG in pyrolysis of poultry litter with banana peduncle. The biochar yield was increased due to the thermal resistance of PG, a mineral that undergoes moisture loss upon heating to 700°C and subsequently transforms into anhydrite (CaSO₄). This transformation led to a co-pyrolysis biochar yield exceeding 40% compared to the biochar yield of animal manure.

The C, H, and N content decreased after mixing the pyrolytic samples, reported C with 27.32% in SS and 17.62% in BA, H content in SS was 4.76% and 4.53% of N, whereas the S content increased with the pyrolytic mixture with more than 8% across all mixture. According to the finding of Wang et al. (2019) study on co-pyrolysis of sewage sludge and cotton stalks at 650°C, reported the C, N and H content of the biochar increased while N contents decreased as the mixing ratio increased. The polymerization/condensation reactions that followed the H-depleting decarboxylation reactions led to the enrichment of C. A similar outcome was observed with co-pyrolysis of sawdust and sewage sludge (Huang et al., 2017) .

The initial content of potential toxic elements in the feedstocks is observed to be increased following the process of pyrolysis, reported the highest value of arsenic from FGDG 114.88 mg/kg at 500°C, then decreased to 108 mg/kg at 900°C, like SS the arsenic level reducing from 7.21 mg/kg at 500°C to 6.28 mg/kg at 900°C. The reduction of arsenic level happened in FGDG and SS, while BA increased the value with increasing temperature (8.81 mg/kg at 500°C, 13.18 mg/kg at 900°C). For arsenic in PG at 500°C remain to be lower than limit of detection then increases to 5.47 mg/kg at 900°C. Similar phenomenon was found in FGDG by Samuel (2021),

recorded higher content of arsenic with 157 mg/kg at 600°C, 39 mg/kg at 800°C, indicating a decrease in arsenic content with increasing pyrolysis temperatures.

In the initial biomass ash, the content of cadmium was 3.26 mg/kg, which was below the limit of detection in PG. Similarly, the biochar produced from biomass ash at a temperature of 900°C also exhibits Cd level below the limit of detection. However, increased contents of Cd were found in biochar produced at 500°C. Contrarily, further increase in pyrolysis temperature to 900°C led to a loss of Cd content. Cadmium level in sewage sludge remained at 900°C (0.16 mg/kg), and 1.12 mg/kg at 500°C. The initial Pb content was 22.55 mg/kg and 18 mg/kg for SS and BA, and decreased to 4.82 mg/kg for SS, 9.78 mg/kg for BA at temperature 900°C. In the study conducted by Murillo (2019), it was observed that the pyrolysis of sewage sludge resulted in Pb content of 8.36 mg/kg at fast rate of temperature 600°C, 700°C and 800°C, and 54.2 mg/kg at a slow rate of temperature 800°C, the oxidable fractions show that Cu and Pb are predominant, indicating that these elements primarily bind to sulphides and organic matter.

The interaction between mixture and temperature affects the biochar total content and availability of the element's content. The total content of potential toxic element was found to be higher in the initial feedstock material compared to the feedstock derived biochar. Arsenic was detected at 26 mg/kg in mixture TA at temperature 500°C. However, available content of arsenic was found below limit of detection at temperature 900°C. Regarding the Cr content of SS at 900°C, which is 85mg/kg, while Cr content was found 64mg/kg at 900°C in TD, the high amount of Cr might has affected by the content of Cr in sewage sludge. While the results described by Huang et al., (2017) who obtained 4mg/kg of Cd, 3.8 mg/kg of Cr, 7.3 mg/kg of Pb by pyrolysis of sewage sludge with rice straw at 700°C. Another study of co-pyrolysis sewage sludge and walnut at 500°C influenced the reducing toxicity and risk of heavy metals, which could transform mobile fractions of Cu, Ni, Cd, and Cr to stable fractions by Liu et al., (2017a), similar results are reported by Chen et al., (2020) by the addition of bamboo, sawdust with sewage sludge during co-pyrolysis significantly minimizing their direct toxicity and bioavailability in the biochar.

In the study of Wang et al. (2019) reported the decreased in total content of some element such as Cr, Ni, Cu, Zn, Cd, and Pb in biochar when increasing temperature of pyrolytic mixture can be explained due to the addition of (i) The addition of cotton stalks reduced the total content of heavy metals due to the "dilution effect"; (ii) Some of those metals transferred into the bio-oil and bio-gas during the pyrolysis process. The reduction of the heavy mental toxicity and risk was affected by the co-pyrolysis of sewage sludge and walnut at 500°C, which changed the mobile fractions of Cu, Ni, Cd, and Cr into stable fractions was reported.

The comparison of potential toxic element in pyrolytic biochar with the Council Directive 86/278/EEC (Council Directive, 1986) on limit value of heavy metal content in sludge use for agriculture, the content of As, Cd, Cu, Cr, Pb, Ni and Zn in sewage sludge biochar are below the control standards limit of heavy mental for agriculture use.

The total content of Ca, P, S and K following pyrolysis process were found to increase as the temperature rose. At 900°C, the pyrolyzed mixture TD produced a higher for P at 56 g/kg and K

at 84.75 g/kg, while S was 95.46 g/kg in TA. The result reported by Wang et al., (2019), the co-pyrolysis of sewage sludge and cotton stalks at 650°C, it was found the application rate of biochar had a significant increase in soil pH, phosphorus, potassium, and Sulfur content.

The ash content of the sewage sludge enriched the nutritive elements K, P, Ca, and Mg. The potential benefits of biochar containing such high content of these nutrients may result in reduced fertilizer consumption and complete replacement of conventional fertilizer sources. Biochar which has a high ash content typically exhibits higher pH value and supply significant amounts of base cations, which can reduce Al^{3+} toxicity in soil, raise soil CECs, and neutralize soil acidity. These mineral nutrients are beneficial for improving nutrient supply and retention in biochar-treated soil (Wang et al., 2019).

Regarding the available content of the initial feedstock, biomass ash contained a high content of K (267.19 g/kg) and S (63.29 g/kg), while sewage sludge contained 8.65 g/kg of P. The pyrolyzed mixture TA exhibited the greatest value of P (4.9 g/kg) and K (70.53 g/kg) at 500°C. Additionally, Ca was reported to be 125.67 g/kg, Mg at 6.12 g/kg and S at 91.22 g/kg at 900°C. In contrast, the availability content of these elements is remarkably similar to those of TB, while TD has the lowest content of S (37.25 g/kg, P (0.321 g/kg) at 900°C.

The assessment of available P, K, and S content in TA at 500°C revealed the following 13% for P, 88% for K and 102% for S, has also reported by European Biochar Industry Consortium (2023) that pyrolysis conducted at temperatures ranging from 500°C to 800°C stand out the most environmentally efficient option. The untreated biochar produced at 400°C, 600°C, and 800°C contained 14-15.53%, 1.88-2.27%, and 3.75-4.77% of K, P, and S contents respectively, while the treated biochar was reported value of 15.21–18.43%, 2.05–2.91% and 0.62–1.09% respectively (Ray et al., 2023).

According to Vimal (2022), the initial release of P from biochar has ability to enhancing seed germination, increased nutrient use efficiency, and decreased leaching loss. The quantity of K, P, and S within the biochar, as well as their release characteristics, predominantly depend on the thermal stability of their mineral phases. These nutrients are sequestered in the biochar in various mineral forms, such as $K(H_2PO_4)_4$, $KH_5(PO_4)_2$, $K_2CaP_2O_7$, KP/K_3P , K_2SO_4 , P_2S_5 , and K_2S/K_2S_5 , with a tendency to exist in water-soluble states (Ray et al., 2023).

Regarding the ANOVA conducted to analyse the effect of temperature and pyrolytic mixture on total content of the element revealed that certain elements including K, Cd, Cr, Pb, Fe, Ni and Zn, exhibited a significant affected by the temperature. However, nutrient elements including Ca, Mg, S, Mn, and Cu exhibited different behaviour concerning both temperature and the pyrolytic mixture. Nevertheless, it was observed that the available content of As, Ca, Mg, and P varied considerably regarding temperatures and pyrolytic mixture. Certain elements, such as Cd, Cr, Pb, K, Fe, Mn, Ni, and Zn, exhibited different results of their content within the temperature range. For instance, the content of Ca, Mg, S and Cr decrease as the temperature rise 500°C to 900°C.

In accordance with Decree No. 474/2000 Coll., the limit value of hazardous elements in fertilizer according to Czech Republic regulation: For As, the limit of presence is 20mg/kg, which is lower in TD after pyrolyzed at temperature 500°C, while TA and TB recorded higher content at both temperatures. For Cd, the limit value is 1 mg/kg, while the analysis has recorded lower content in the pyrolyzed mixtures at 900°C and exceeded the limit value at 500°C for all pyrolyzed mixtures. On the other hand, the limit value of Cr is 50 mg/kg, which is lower than pyrolyzed mixture TB and TD at 500°C, while for TA was found higher at 500°C (54 mg/kg) and 900°C (63 mg/kg). Moreover, the limit of presence for Pb is 10 mg/kg, which is much lower than the feedstocks mixtures after pyrolysis process.

7 Conclusion

Co-pyrolysis of sewage sludge (SS), biomass ash (BA), flue gas desulfurization gypsum (FGDG) and phosphogypsum (PG) at different ratios and combinations, was done at two different temperatures 500°C and 900°C for 30 minutes. Biochar derived from pyrolysis was analysed to determine the total and available content of elements.

During co-pyrolysis, biochar yield was produced from mixtures TA (combination of SS, BA, FGDG, PG), TB (combination of SS, BA, FGDG, PG), and TD (combination of SS, BA, and PG), with decreasing trend in yield observed as the temperature increased. In the case of mixture TA, the biochar yield decreased from 71% at 500°C, to 47% at 900°C, while TD exhibits the lowest yield decreased from 69% at 500°C, to 45% at 900°C.

The total content of potential toxic elements after analysis shows the highest levels presence in TA such as As, Cr, Cd and Pb. For Cr is notably lower at 500°C in TB and TD, while As was recorded to have the highest value presence in TA with 26 mg/kg at both temperatures, which is 4 times lower than the As reported in FGDG. However, it is reported that pyrolyzed feedstocks contained low content of Pb (13.80-16.53 mg/kg) and Cd (0.46-0.60 mg/kg) at 900°C, these elements was present in the initial feedstocks at 22 mg/kg of Pb and 3.26 mg/kg in SS respectively. In contrast, Cd and Pb decreased as the temperature of pyrolysis increased to 900°C, while As and Cr exhibit the lower content at 500°C. The availability of potential toxic elements was observed to decrease with pyrolytic temperature especially for As and Cr were below detection limits at 900°C for all pyrolyzed feedstocks.

The available content of some elements in pyrolyzed feedstocks including Ca, K, P, S, and Zn were decreased with increase temperatures, while Cu and Ni were below detection limit at 900°C. For micronutrients like Fe, and Mn, they were increased with increasing temperature. However, Ca, K, P, and S in TA had the highest content at 500°C, while Mg and P didn't increase much during the pyrolysis compared to the feedstock materials. The feedstocks pyrolyzed at temperature 500°C and 900°C confirmed the valorisation of P, K and S, suggested to be greater in TA. The pyrolyzed feedstocks (TA) derived biochar had higher levels of P (54 g/kg) and S (95.46 g/kg), while resulting of K content of 84 g/kg in TD.

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