agronomy

Review

Soil Nitrogen Sorption Using Charcoal and Wood Ash

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Abstract: This paper reviews the use of charcoal and wood ash in acid soils as adsorbents to improve N availability at the same time improving their soil fertility and crop productivity. Soil acidification poses a major challenge in agricultural sustainability and it is serious in highly weathered soils such as Ultisols and Oxisols which are noted for nutrient deficiency and Al and Fe ions toxicities. Understanding sorption mechanisms and isotherms is important for the improvement of soil N availability particularly inorganic N. However, understanding the sorption mechanisms in relation to charcoal and wood ash as absorbents in the literature is difficult because the soil amendments vary depending on their raw materials or sources of origin. Therefore, one of the objectives of this review is to provide recent research findings and theory development on the role of charcoal and wood ash in agriculture. Furthermore, this review focuses on how charcoal and wood ash improve N availability through physical, chemical and biological processes in mineral acidic soils. Balanced application and good understanding of the role of charcoal and wood ash as soil amendments have potential benefits to improve N availability and crop productivity.

Keywords: nitrogen mineralization; nitrogen availability; organic amendments; mechanisms; soil acidity

Citation: Hamidi, N.H.; Ahmed, O.H.; Omar, L.; Ch'ng, H.Y. Soil Nitrogen Sorption Using Charcoal and Wood Ash. *Agronomy* **2021**, *11*, 1801. https://doi.org/10.3390/agronomy11091801

Academic Editors: Alwyn Williams and Baskaran Stephen Inbaraj

Received: 3 May 2021
Accepted: 6 July 2021
Published: 8 September 2021

1. Introduction

Views have been expressed that by 2050, approximately 70% to 100% increase in the worldwide agricultural production will be needed to feed nine billion people in the world [1]. To achieve the world-wide sustainable food supply that can cope with the rapid urbanisation and growth of the human population, optimum use of fertilisers is essential [2]. Anthropogenic activities such as rapid industrialisation and intensive agricultural production with substantial amount of N fertilisation causes losses of C and N to the environment [3]. Nitrogen fertilisers are highly mobile in soils and because of this, they should be carefully used in agriculture to avoid losses through volatilisation, denitrification and leaching [4]. Poor synchrony of fertiliser nutrient release for timely uptake by plants also contributes to significant loss of N-based fertilisers in most farming systems. Moreover, high temperature and heavy rainfall cause poor nutrient use efficiency in highly weathered acid soils. These activities lead to low nutrient content and rapid mineralisation of soil organic matter [5]. Soil acidification poses a major challenge to agricultural sustainability [6]. This problem is particularly serious in highly weathered soils whose supply of most plant nutrients apart from Fe, Al, and Mn ions decrease with increasing pH. For example, as base cations such as K, Ca, Mg, and Na acquire leached from highly weathered soils, these nutrients including NH_4 and NO_3 ions are replaced by Fe, Al, and Mn ions. In addition to loss of organic matter, and Fe and Al hydrolysis result in further soil acidification which decreases soil productivity.

Approximately 90% of the soil total N is composed of organic N which plays an important role in N transformation and retention [7]. In addition, approximately 90% of the N fertilisers in the world is in the inorganic form (NH_4^+). The ammonium ions are transformed into highly mobile NO_3^- and NO_2^- by nitrifying bacteria under aerobic conditions in soils [8]. Nitrogen leaching and runoff do not only reduce nutrient uptake efficiency, but also cause serious environmental pollution such as eutrophication [8]. One of the approaches to solve this problem is controlling the dissolution and hydrolysis of N fertilisers such as urea, ammonium nitrate, ammonium sulphate, among others. This practice controls the availability of urea-N by reducing the microsite pH with acid materials such as acidic phosphates and phosphoric acid [9,10]. However, these materials are expensive and corrosive.

Another approach to minimise nutrient losses is through for example, treating poultry manure which is co-composted with rice husk bio-charcoal (RHC). This RHC is able to reduce N losses because it traps organic and inorganic nutrients such as C, N, P and K to prevent them from being leached from soils [11]. However, this method is time consuming. Thus, efforts are on-going to increase the ability of organic amendments, not only for improving soil productivity but also to improve chemical fertilisers use efficiency [12]. The use of composts, manures, and mulches has proven to improve soil fertility. However, in the tropics, organic matter mineralises rapidly [13] and only a small amount of the organic matter applied is stabilised in soils for a long period [14]. Therefore, it is essential to control N losses to enhance N retention using inexpensive, reliable, and environmentally friendly methods, one of which is using charcoal and wood ash.

Charcoal is a solid carbonaceous residue which is produced by heating through slow and rapid pyrolysis, gasification, and hydrothermal carbonisation under oxygen-deficient conditions [15]. Charcoal is produced through slow pyrolysis [16] and it is highly resistant to decomposition [17,18]. Charcoal in soils does not only influence the nature of sorption mechanism but it also improves sorption of organic pollutant [19,20]. Charcoal can play an important role in soil physical, chemical and biological processes at least for the first few decades after its formation [17,21,22]. In carbonaceous materials, adsorption is regulated by physical and chemical structures [20]. Adsorption is commonly used as an efficient physical separation mechanism to remove or reduce the concentration of several dissolved contaminants whether organic or inorganic pollutants [23]. The charcoal structure reflects the morphology of the raw material used [24]. A typical charcoal consists of C, H, N, S, ash, and oxygen [25]. In addition, its structure, composition, and characteristics such as particle size distribution, moisture content, density, ash content, and pH depend on the form, nature and origin of raw material, along with the state of thermal conversion cycle [26]. Charcoal is made up of several inorganic and organic forms of N and P, such as NO_3^-, NH_4^+, amide groups and ortho-P [27,28]. However, the concentrations of these nutrients depend on production temperature and source of the charcoal. For example, charcoal produced at lower temperature have more NH_4^+, whereas charcoal produced at higher temperature tends to have more NO_3^-. Charcoal produced from plant residues usually has higher nutrients than charcoal which is generated from ligno-cellulosic raw materials [29]. The contents of the nutrients, and the conservation of nutrients can be enhanced by applying charcoal to soils. This is particularly relevant in heavily weathered soils with poor ion retention capacity [30]. Furthermore, C materials are resistant to toxic conditions and corrosive environments such as basic and acidic conditions because of their unique structure and electrical conductivity [31].

Van Laer et al. [32] reported that wood ash can be used as soil conditioner. Wood ash which is produced through combustion is not only alkaline, but it also contains high amounts of soluble macronutrients such as Ca, K, P, and Mg [33]. Moreover, wood ash has the potential to reduce nutrient loss from crop harvesting and it is ideal for acid soils that are highly weathered because of its acid neutralising capacity. Base saturation and microbial activities increase with decreasing soil acidity [34]. However, with time, the effects of wood ash as a soil amendment reduces because of the biogeochemical interactions between amendment and soil profile [35,36]. The adsorption properties of wood ash are influenced by its specific surface area. Apart from its specific surface area, particle size distribution, pore size and pore volume are important physical properties that influence the use and quality of C residues or ashes as an adsorbent [37]. Furthermore, the use of wood ash can increase water holding capacity, moisture content, and nutrient availability because its hydrophilic property enables it to retain water [38]. However, understanding the sorption mechanisms derived from literature is difficult because charcoal and wood ash as adsorbents vary depending on the raw materials used in their production. Therefore, the goal of this review is to provide the recent research findings and theory development on the role of charcoal and wood ash in agriculture. The specific objectives of this work are to discuss the: (1) effects of charcoal and wood ash on the sorption behaviour of inorganic N, and (2) mechanisms that can be used to improve N availability by charcoal and wood ash. In summary, this review focuses on how charcoal and wood ash improve N availability through physical, chemical and biological processes in acidic mineral soils.

2. Acidic Soils of Malaysia

Soils in the humic tropics (especially those under high temperature and rainfall throughout the year) are highly weathered because they exist in tropical environment, causing accumulation of sesquioxides and leaching of plant nutrients [39]. For example, approximately 72% of the land in Malaysia are Ultisols and Oxisols with goethite, kaolinite, gibbsite, and hematite in the clay fraction [40]. Lack of essential nutrients, mineral toxicities, and reduced water uptake are constraints to production in acid soils with preliminary visual symptoms of reduced root length on plant growth [41]. Naturally, because these types of soil lack available P, Ca^{2+}, and Mg^{2+}, their productivity is low. Furthermore, nutrient availability is closely related to soil pH. Low pH affects availability of macronutrients to cause their deficiencies. In most cases, Al^{3+}, Mn^{2+} and H^+ toxicities and nutrient deficiencies limit the productivity of acidic soils. Low mineral content and rapid mineralisation of organic soil materials are constraints on sustainable tropical agriculture [13,42]. Application of acidic N fertilisers, N transformation such as nitrification that produces H^+ ions and other reactions of releasing H^+ ions into the soil contribute to soil acidification [43]. Commonly, this problem is overcome by using a liming material such as ground magnesium limestone [44] because liming increases soil pH, Ca^{2+} and Mg^{2+}, base saturation, soil available nutrient, organic matter, and microbial activity. However, a liming material such as limestone is limited and expensive. Additionally, because tropical soils are low organic matter, improving their fertility, alternative soil amendments from agricultural wastes such charcoal and bark ash can be used because these wastes are abundant and readily available. In the tropics, organic amendments are used to restore soil fertility, particularly Ultisols and Oxisols by improving their chemical properties and nutrient bioavailability [45,46].

3. Soil Acidification

Soil acidification poses a major challenge to agricultural sustainability [6]. This problem is particularly serious in highly weathered soils whose supply of most plant nutrients apart from Fe, Al, and Mn ions decrease with decreasing pH. For example, as base cations such as K, Ca, Mg, and Na acquire leached from highly weathered soils, these nutrients including NH_4^+ and NO_3^- ions are replaced with Fe, Al, and Mn. Hydrogen ions derived from N fertilisers such as urea particularly NH_4 ions as a source of N release two H^+ ions for each conversion of NH_4^+ ions to NO_3^- [47]. In addition to losing soil organic matter, Fe and Al hydrolysis which lead to further soil acidification, the fertility of Ultisols and Oxisols are decrease with time. During the decomposition of soil organic matter (depending on the organic matter derived), the organic acids produced affect soil acidity. If the decomposed plant does not have sufficient bases to fulfil microbial needs, the decomposition of plant debris will not only produce carbon dioxide, but it will also remove essential bases such as Ca^{2+} and Mg^{2+} from the soil [47].

4. Forms of Nitrogen in Soil-Plant Systems

Approximately 90% of the soil total N is composed of organic N which plays an essential role in N transformation and retention [7] and 90% of the N fertilisers in the world is in the inorganic form of NH_4^+. The NH_4 ions are transformed into highly mobile NO_3^- and NO^{2-} by nitrifying bacteria under aerobic conditions in soils [8]. Nitrite and N_2O are present in small quantities in soils. Commonly, N is considered available if it can be taken by plants. The uptake of N from soils by plant roots is mainly in the forms of NH_4^+ and NO_3^- because organic N is mostly unavailable for direct plant uptake. Soil properties including pH, texture, moisture and microbial activities influence N availability which commonly fluctuates significantly in both time and space [48]. At any given time, approximately 95% of the potentially available N in the soil is in organic form whether in plant and animal residue, bounded with organic matter, small animals or microorganisms [49]. This conversion is carried out by microorganisms as they decompose soil organic matter or residue from forest litter, previously grown crops and pastures. During decomposition, N can be immobilised from plant-available forms or mineralised into plant-available forms. The mineralisation rate depends on environmental factors such as temperature, moisture content, type or amount of organic N present. The ratio of C to N in residues is a deciding factor as to whether N is released or removed in the soil [50]. Soil N fractions are divided into inorganic and organic N fractions.

5. Nitrogen Fractions and Pools in Soils

Nitrogen often transforms in different forms [51]. The major forms of N include N source from organic matter, which is organic N and inorganic sources of N such as NH_3, NH_4^+, NO_3^- and N_2 gas. According to Brady and Weil [52], an atom of N can appear in different chemical forms each with its own properties, behaviour and significance for the environment. Korhonen et al. [53] opined that, despite the large pool of total N, mineral N concentrations are usually low compared with the ecosystem productivity and plant uptake which are limited by the availability of N indicates that the organic N availability is poor for plants and microorganisms.

Labile soil N fractions that transform rapidly during crop growing season are indicated by microbial biomass N, a measure of N immobilisation and potential N mineralisation [54]. A measure of N storage in coarse organic matter known as particulate organic N is an intermediate fraction between slow and labile fractions which is also transformed rapidly during growing season [55]. This intermediate fraction is an essential substrate for soil microorganisms [55]. The available N fraction is the soil mineral N such NO_3^- and NH_4^+, either taken up by plants or lost to the environment [56,57]. The origin and importance of N fractions in the soil N cycling is replete in the literature [58–60]. Nonetheless, whether organic N fractions such as microbial biomass N and soil organic N, and inorganic N exhibit synchronous patterns during N transformation in soils and how this process is affected remain uncertain [7].

6. Soil Organic Nitrogen

Schulten and Schnitzer [61] stated that organic form of N is a dominant component of soil N. Organic N fractions consist of acid-insoluble and acid-hydrolysable. Amino acids, amino sugar, ammonium and other unknown N sub-fractions are acid hydrolysable components [7]. Schulten et al. [62] revealed that most soil organic N is proteinaceous material or heterocyclic including purines and pyrimidines. Soil organic N primarily occurs as biogenic polymers that varies in decomposition state. The main building block of protein is the α-amino acids, which makes up 50% of microbial biomass [63], and major component of soil organic N [64]. Moreover, amides consist of α amino-N, peptides contain less abundant non-α amino-N moieties. Amino sugar is the second most abundant component of soil organic N, the principal of microbial cell walls N-containing components [64,65]. Chitin is the main amino sugar polymer in fungal cell walls, whereas bacterial cell walls have a peptidoglycan layer composed from α-amino acid and bacterial amino sugar. Shmidt et al. [66] reported that decomposition of soil organic matter or soil organic N is regulated by several processes and factors such as molecular structure, condensation reaction, rhizosphere input, soil depth, freezing-thawing, residues and microbial products. On the whole, multiple processes which preserve and release N from soil organic matter significantly affect soil C and N cycling.

Primarily, organic N is in the form of urea and amino acids, along with proteins and peptides [67]. Fulvic and humic substances also contribute to the pool of dissolved organic N. However, proteins and peptides in the soil are decomposed by protease secreted by soil microorganisms into their constituent amino acids units [67]. Organic N form in soils is divided into two categories: (i) organic residues including partial decomposition product and un-decayed plant and animal residues, and (ii) soil organic matter and humus. The humus consists of humic substances that are high in molecular weight. They are partly aromatic substances formed by secondary reaction, amorphous and non-humic such as chemically recognisable substances (nucleic acids, amino acids and carbohydrate) [58]. Throughout the decomposition of organic matter by soil microorganisms, excess N is transformed to NO_3^- and NH_4^+. When organic matter is rich in N, mineralisation occurs. Ashton et al. [68] reported that, when organic N undergoes mineralisation to inorganic N, it is taken up by plants easily. Mineralisation is a process when microorganisms convert organic N to inorganic forms. However, degradation of organic matter with low N content causes immobilise NH_4^+ and NO_3^- because degrading microorganisms scavenge available N from soil systems [69]. Vigil and Kissel [70] reported that degradation of organic materials with a C:N ratio more than 40:1 immobilises N, whereas decomposition lower than this ratio mineralises N. Thus, the rate of organic N mineralisation is an essential factor controlling ecosystem productivity [71]. According to Walworth [69], mineralisation can be divided into ammonification (Equation (1)) and hydrolysis (Equation (2)), where organic N is converted to NH_3 and the conversion in water of NH_3 to NH_4^+.

Ammonification:

$$\text{R-NH}_2 + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{R-OH} + \text{energy} \tag{1}$$

Ammonia hydrolysis:

$$\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH} \tag{2}$$

7. Soil Inorganic Nitrogen

Hawkins and Robbins [72] described that, NH_4^+ and NO_3^- are prevalent inorganic forms of N which are commonly taken up by plants. The major form of inorganic N in aerobic soils is NO_3^- whereas NH_4^+ is the major form in acidic soils or flooded wetland [73].

8. Soil Inorganic Nitrogen (Nitrate-Nitrogen)

Nitrate is a negatively-charged ion, thus it is difficult for NO_3^- to form surface complexes with soil particles. Nitrate salts are mobile with soil water, highly soluble and prone to leaching if not utilised by microorganisms or taken up by plants [52,74]. According to Walworth [69], denitrification reduces NO_3^- to N_2O or dinitrogen gas (N_2) by anaerobic bacteria (Equation (3)):

$$2\text{HNO}_3 \rightarrow 2\text{HNO}_2 \rightarrow 2\text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2 \tag{3}$$

Furthermore, this reaction is the primary mechanism for N loss when soils are saturated with rain, waterlogged condition or poorly aerated soils. Organic matter provides energy and C for denitrifying bacteria through oxidation and NO_3^- acts as the terminal electron acceptor [69].

9. Soil Inorganic Nitrogen (Ammonium-Nitrogen)

Ammonium is the predominant source of N that is available for plant nutrition although the average of NH_4^+ concentration of soils is often lower than NO_3^- [75]. However, when plants are grown in soils with high amount of NH_4^+ in the absence of NO_3^-, toxicity symptoms occur except rice, onion, leek, blueberry and cranberry which prefer NH_4^+ [76].

In addition, NH_4^+ ion in neutral to acidic water, and under high pH, it is converted to NH_3. At pH 9, approximately half of the NH_3 is in gaseous and less than 10% of it is in gaseous form below pH 8 [77]. Ammonium is attracted to the negatively charge soil particles because of its positive charge, thus it is held as exchangeable cation in soils and it does not leach easily. Moreover, NH_4^+ can be trapped between the layers of clay minerals that exhibit swelling and shrinking through NH_4^+ fixation [52,69].

The NH_4^+ is rapidly oxidised to NO_3^- under sufficient oxygen condition through nitrification because it is relatively unstable in aerobic soils. During nitrification, the conversion of NH_4^+ takes place in two steps and they are the conversion of NH_4^+ into NO_2^- by *Nitrosomonas* (oxidising bacteria) (Equation (4)), and the oxidation of NO_2^- to NO_3^- by *Nitrobacter* (Equation (5)).

First step of nitrification:

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+ \tag{4}$$

Second step of nitrification:

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \tag{5}$$

As demonstrated by Walworth [69], nitrification causes soil acidity through production of large amount of H^+ ions and oxidation of NO_2^-, and because this reaction occurs rapidly, NO_2^- rarely forms inorganic soil N.

10. Nitrogen as a Fertiliser

Because N forms are easily converted in soils, the choice of N fertiliser is based on cost [69]. Nitrogen fertilisers are classified as organic or chemical, the latter being highly soluble when applied to soils [78]. The use of synthetic N fertilisers has reduced major elemental constraints to supply organic C and N originally managed by organic manure amendments, leguminous culture and uncultivated periods [79]. The common fertilisers are listed in Table 1 Urea is the most used solid N fertiliser because it can be easily handled, stored, transported, and produced [80].

Table 1. Some commonly used nitrogen fertilizers [69].

Fertiliser	% Nitrogen	Composition
Ammonium sulfate	20.5	$(NH_4)_2SO_4$
Calcium nitrate	16	$Ca(NO_3)_2$
Urea	45	$(NH_2)_2CO$
Anhydrous ammonia	82	NH_3
Diammonium phosphate	20	$(NH_4)_2HPO_4$
Ammonium polyphosphate	10–15	$(NH_4PO_3)_n$
Urea ammonium nitrate	28–32	$(NH_2)_2CO$, NH_4NO_3

11. Urea

Urea, the world's most common solid N fertiliser is a white crystalline organic chemical, and it is also known as carbamide (NH_2CONH_2). Among the other solid sources of N available in the market, urea has the highest N content (46% N). Synthetic urea is manufactured from NH_3 and carbon dioxide under high pressure and moderate temperature with the help of suitable catalyst [78,81].

$$2NH_3 + CO_2 \rightarrow NH_2COONH_4 \tag{6}$$

Ammonium carbamate which is produced is relatively an unstable intermediate, and with time decomposed urea is recovered. Thereafter, 99% concentrated urea solution is sprayed into a chamber where urea crystals are formed [78].

$$NH_2COONH_4 \rightarrow NH_2CONH_2 + H_2O \tag{7}$$

The NH_3 needed for urea manufacturing is made by combining one mole of N with three moles of hydrogen with iron oxide (Fe_3O_4, FeO) as a catalyst. In addition, urea is a simple organic N salt which is highly soluble, but it must be hydrolysed by enzyme called urease to form NH_4^+ before it is utilised (Equation (8)). If urea or ammonium fertilisers are used at pH 8 or above, NH_3 volatilisation causes loss of N especially if the fertiliser is not incorporated into the soil immediately after utilisation to prevent loss. During urea hydrolysis, soil pH increases rapidly and substantial N is lost through volatilisation even in medium pH soils [69].

Urea hydrolysis:

$$CO(NH_2)_2 + 3H_2O \rightarrow 2NH_3 + CO_2 + 2H_2O \rightarrow 2NH_4^+ + CO_2 + 2OH^- \quad (8)$$

Currently, a significant amount of urea fertilisers are applied onto agricultural land resulting in soil acidity, leaching of NO_3^- and environmental pollution such as eutrophication [82].

12. Role of Nitrogen in Crops Productivity

Kusano et al. [83] described N as one of the most essential nutrients for biomass production and plant growth that is involved in the synthesis of nucleic acids, amino acids, lipids, chlorophyll and various N-containing metabolites. Nitrogen is one of the most widely used nutrients, because plants need N in the largest quantity compared with other mineral elements such as P and K [84]. Nitrogen deficiency is a limiting element for plant growth and development [85–88] including root architecture [89], leaf development [90], flowering [91], and seed dormancy [92].

13. Nitrogen Availability in Soils

Nitrogen is considered available if it is vulnerable to plants uptake. However, there is no sufficient information about the quantitative measurements of available N or N availability and the terms of available N and N availability in definition [93]. Nitrogen in a chemical form that can be readily absorbed by plant roots is called available N. In another words, available N is the N that is present within the root zone of plants [94]. The processes that contribute to available N supply in soils are organic matter, addition of fertilisers, symbiotic fixation, non-symbiotic fixation and rainfall. Nitrate and exchangeable NH_4^+ in a rooting depth of a crop are directly available to plant roots in arable soils. In the tropics, management of N is essential because providing much of this element can become unavailable [95].

14. Factors Affecting Nitrogen Availability to Crops

Soil drainage, texture, and slope steepness affect N transport and transformation, utmost accessibility thus leading to losses. Moreover, soil aeration, electrical conductivity, rainfall, temperature and moisture affect the rate of N mineralisation and nitrification affecting osmotic potential and altering substrate availability from decomposition of organic matter [96], nutrient cycling and N losses through denitrification, leaching and surface runoff. Decomposition of organic matter releases N rapidly in well aerated soil, and humid climate because soil climatic conditions affect biomass and microbial activities [97]. Abera et al. [98] stated that vegetation also affects nitrification and mineralisation through the amount and quality of litter. Soil moisture is the most crucial factor that limits microbial activities because in the tropics, temperature is not a limiting factor. Maximising N accessibility from autochthonous soil N and supplemental N from manures, fertilisers or compost to optimise yield is the initial requirement for understanding N availability [69].

15. Nitrogen Transformation in Soil-Crops Systems

Anthropogenic activities such as rapid industrial development and intensive agricultural production with a substantial amount of N fertilisation cause losses of C and N to the environment [3]. Nitrogen fertilisers are highly mobile in soils and because of this, they should be carefully used in agriculture to prevent losses through volatilisation, denitrification, and leaching in particular [4]. Apart from poor synchrony of fertiliser nutrient release for timely uptake by plants, the problem of inefficiency of these fertilisers is compounded in highly weathered acid soils which are low nutrients and rapid mineralisation of soil organic matter because of high rainfall and temperature [5]. Nitrogen losses from agricultural systems via denitrification, volatilisation and leaching have negatively impacted the atmosphere, surface and ground water, and uncultivated ecosystem. Approximately 90% of the soil total N is composed of organic N which plays an important role in N transformation and retention [7]. If the N applied is not taken up by plants or immobilised in soil organic N pool, it is prone to losses from emissions of N_2O and NO following nitrification-denitrification process, leaching of NO_3^-, volatilisation of NH_3, all of which can have a range of undesirable on-site and off-site environmental outcomes [99]. Understanding N transformations and soil microbes is important for understanding and managing ecosystem health and productivity. Nitrogen takes nine forms in soils equivalent to different oxidative state in (Table 2) [100].

Table 2. Main Forms of Nitrogen in soils and their Oxidation State.

Name	Chemical Formula	Oxidation State
Nitrate	NO_3^-	+5
Nitrogen dioxide [g]	NO_2	+4
Nitrite	NO_2^-	+3
Nitric oxide [g]	NO	+2
Nitrous oxides [g]	N_2O	+1
Dinitrogen [g]	N_2	0
Ammonia [g]	NH_3	−3
Ammonium	NH_4^+	−3
Organic N	R_{NH3}	−3

Gases (g) occur both free in the soil atmosphere and dissolved in soil water.

16. Mineralisation and Immobilisation

In older literature, mineralisation is known as ammonification because NH_4^+ is viewed as immediate product of mineralisation. According to Myrold et al. [101], mineralisation is the production of inorganic N from organic N whereas immobilisation is the assimilation of inorganic N into organic forms. Globally, soil N mineralisation rates are believed to be controlled by climate and soil properties [102]. Mineralisation is suppressed by soil acidification [102]. However, addition of organic matter and soil substrate increase N mineralisation [103,104]. Soil fauna such as several microorganisms including fungi, aerobes and anaerobes bacteria play an essential role in these processes. They are responsible for decomposition of wastes, for microorganisms to populate, indirectly creating a suitable environment for micro-fauna such as earthworm, and termites. These two processes are fundamental because a by-product of all heterotrophic soil organisms consume organic materials for C and energy [100]. Mineralisation and immobilisation occur simultaneously within the small volume of soils; thus, it is important to differentiate these two processes. Moreover, mineralisation results in increasing inorganic N, whereas immobilisation decreases N. It is important to make a distinction between gross and net mineralisation and immobilisation as a result of the simultaneous nature of these processes. Furthermore, the total amount of soluble N produced by microorganisms is gross N mineralisation, whereas the total amount of soluble N consumed is gross N immobilisation. Net mineralisation is when gross mineralisation exceeds gross immobilisation resulting in inorganic N availability. On the other hand, net immobilisation is when gross immobilisation exceeds gross mineralisation resulting in decreasing amount of inorganic N [100]. According to Follet [49], mineralisation is when NH_4^+ is released. In sufficient oxygen, microorganisms in the soil convert NH_4^+ ions to NO_3^- ions with NO_2 as an intermediate form (nitrification). Addition of charcoal and wood ash as amendments affect the C:N ratio and generally immobilisation of N occurs when the C: N ratio increases [105].

17. Nitrification

Nitrification is a process when NH_4^+ is converted to NO_3^- [49,106]. Thus, nitrification is the microbial oxidation process of reducing N to NO_3^- ions and NO_2^- ions [100], carried out by two different groups of microorganisms specifically autotrophic and heterotrophic nitrifiers, and is crucial and useful parameter of the soil environment [107]. In most ecosystems, NO_3^- is formed in situ through nitrification, although some NO_3^- is supplied as fertilisers or acid rain. Nitrate is more mobile than NH_4^+ because of its negative charge, and the ionised source of NH_3 in soil water is demonstrated in Equation (9) [100]:

$$NH_4^+ \text{ (aq)} \rightarrow NH_3 \text{ (aq)} + H^+ \text{ (aq)} \tag{9}$$

Ammonium ions are held on cation exchange sites associated with clay surfaces, organic matter and variable-charge mineral because of their positive charge, whereas NO_3^- is transported out of roots zone when precipitation exceeds evapotranspiration and also, they are prone to denitrification. Denitrifying bacteria transforms NO_3^- to N gas [100]. In a short-term field experiment, Berg and Roswall [108] demonstrated that nitrification potential, clay mineral content and amount of NH_4^+ oxidisers increased with increasing soil moisture. Macura and Stotzky [109] adds that after the addition of montmorillonite, nitrification rate was higher. In many soils, nitrification is the major source of acidity, including hydrologic loss of base cations as H^+ displace other cations from exchange sites including mostly in highly weathered tropical soils. Moreover, soil acidity affects soil CEC [100]. Application of amendments such as charcoal, wood ash and biochar promote net nitrification particularly in natural environment because of their liming effect or removal of inhibiting compounds such as polyphenols or tannins [110,111]; although application of amendments such as charcoal, biochar and wood ash may have no significant effect on gross or net nitrification rates in agricultural soils [110,112].

18. Denitrification

Denitrification is conversion of soil NO_3^- to N gases such as NO, N_2O and N_2 [100]. In another study, Follet [49] stated that NO_2^- does not accumulate in soils because it is rapidly denitrified to NO, N_2O and N_2. Additionally, denitrification causes NO_3^- loss to the atmosphere. In addition, Dobrovol'skaya et al. [107] reported that formation of N_2O is common in soils that are structureless, salinised, pH lower than 7, contaminated with pesticides and high in heavy metals. Mostly, heterotrophic bacteria can denitrify N because they use NO_3^- as a terminal electron acceptor during respiration instead of oxygen, and most denitrifiers undertake denitrification only when there is sufficient oxygen because NO_3^- is a less efficient electron acceptor than oxygen. In waterlogged condition, diffusion of oxygen to microsites reduces significantly [100]. Some of the conditions required for denitrification to occur are: (i) presence of bacteria possessing the metabolic capacity, (ii) suitable reductants (organic carbon), (iii) absence or restriction of oxygen and (iv) N oxides availability (NO, N_2O or N_2) (Table 3) [113–115].

Table 3. Factors affecting the proportion of N_2O and N_2 produced during denitrification [48].

Factor	Will Increase N_2O or N_2
NO_3^- or NO_2^-	Increasing oxidant
Oxygen	Increasing oxygen
Carbon	Decreasing C availability
pH	Decreasing pH
H_2S	Increasing Sulfide
Temperature	Decreasing temperature
Enzyme status	Low N_2O reductase activity

However, the end product and the rate of the N_2O producing processes are influenced by conditions and properties of the soil such as organic matter, N, substrate availability and form, pH and oxidative conditions [116].

19. Volatilisation

Volatilisation can occur from surface-applied N sources. Nitrogen loss as NH_3 gas. Liu et al. [117] reported that, NH_3 volatilisation is the main N gas loss pathway and approximately 64% N applied is lost through volatilisation. Ammonia loss occurs when N based fertilisers are used. Ammonia is an intermediate form of N during the process in which urea is transformed to NH_4^+–N. Ammonium ions in the soil solution enter into an equilibrium reaction with NH_3 in the soil solution, whereas significant amount of NH_3 volatilised into the atmosphere can cause air pollution. In addition, N deposition can cause eutrophication thus, destroying biodiversity [118,119]. The important factors that contribute to N losses via NH_3 volatilisation include the activity of enzyme urease, assimilation of ammonia by soil biota, buffering capacity, soil physical properties that control mass flow and diffusion of water and dissolved solutes, and soil pH [120]. Rochette et al. [121] reported that with the equilibrium relationships during experiment between pH, NH_3 and NH_4^+ as pH is increased by urea hydrolysis, the activity of H^+ required to transform NH_3 to NH_4^+ decreased thus and the proportion of NH_3 release to the air relative to the proportion converted to NH_4^+ increased with increasing urea application (Equation (12)). A study in Nebraska found that when urea-based fertilisers are left on the soil surface, the risk of NH_3 volatilisation increased on poorly buffered, coarse textured soils without rainfall to move N seep into soils and when heavy rainfall occurred, the risk of NH_3 volatilisation decreased. However, leaching can occur in these conditions [122]. Stevenson [123] summarised that NH_3 volatilisation is most significant when pH is greater than 7, and the loss is also greater in soils with low CEC. Ammonia loss can increase when organic wastes which are high in pH and N decompose on soil surface. Furthermore, NH_3 volatilisation increases with increasing temperature, principally in alkaline and neutral soil as they become dry and losses are high from urea applied as urease hydrolyses urea to NH_3 gas. Firstly, NH_3 volatilisation involves urea hydrolysis through urease. Urease is an extra-cellular enzyme produced as by product of plant residues or several soil microorganisms [124].

Urea hydrolysis:

$$(NH_2)_2CO + 2H_2O \rightarrow (NH_4)_2CO_3 \tag{10}$$

$$(NH_4)_2CO_3 + 2H^+ \rightarrow 2NH_4{}^+ + CO_2 + H_2O \tag{11}$$

$$NH_4{}^+ + OH^- \rightarrow NH_3 + H_2O \tag{12}$$

In most soils, pH increases to a range of 7 to 9 upon completion of the urea hydrolysis, because one mole of urea molecule utilises two moles of H^+ ions from soil water to produce two moles of OH^- [124]. The increase in pH causes the proportion of N in the form of NH_3 to increase and this increases the risk of NH_3 volatilisation. The efficiency of surface applied urea for N crop uptake reduces because of volatilisation. However, it can be controlled by retarding hydrolysis using urease inhibitors or enhancing NH_4^+ retention formed by urea hydrolysis using amendments with high specific surface area and CEC. This approach does not only enhance NH_4^+ retention but it also improves soil buffering capacity to reduce in pH [125]. This strategy was adopted by Paiva et al. [126] to coat fertiliser granules with oxidised charcoal as a fertiliser amendment because during hydrolysis, N fertilisers such as urea must be in the microsite contact with the oxidised charcoal to maximise efficacy. This oxidation contributes to increase in CEC by increasing the contents of phenolic, carboxylic, N-containing groups, thus, improving in the metal adsorption capacity of charcoal [127].

20. Leaching

Leaching is loss of soluble nitrate because it moves with soil water, commonly excess water below plant root zone through drainage systems. Nitrate that moves below plant root zone has the potential to enter groundwater of surface water because NO_3^- can be leached from any soil if rainfall or irrigation moves water through root zone. According to GDRC [50], several chemical reactions change urea to NH_4^+ to NO_3^- form leading to leaching of NO_3^- from the soil profile. Approximately 90% of the N fertilisers in the world are in the inorganic form NH_4^+. The ammonium ions are transformed into highly mobile NO_3^- and NO_2^- by nitrifying bacteria under aerobic conditions in soils [8]. Nitrogen leaching and runoff do not only reduce nutrient uptake efficiency, but they also cause serious environmental pollution such as eutrophication [8]. Nitrate ions are the primary form of N leached, soluble in soil water and moves freely through most soils [49]. Jury and Nielson [128] stated that the movement of NO_3^- is controlled by mass flow and diffusion within the soil solution. Di and Cameron [129] added that high amount of NO_3^- leaching loss occurs when there is high amount of NO_3^- in the soil profile together with or followed by high drainage volume. Fertilisers, effluents and mineralisation of soil organic N could be some of the sources of NO_3^- [130]. It is well documented that rainfall, irrigation, tile drainage and water table fluctuation influence NO_3^- leaching rate [131]. In addition, fertilisation levels, type of fertiliser, time and method of application, type of plant, agronomic practices and soil properties such as soil pH, soil texture and soil organic matter content influence leaching of NO_3^-.

21. Crop Removal, Soil Erosion and Runoff

Inorganic N can be lost from soil system by plant uptake. According to O'Leary et al. [132], plant removal such as harvesting reduces soil N loss. Foster et al. [133] opined that, soil erosion accelerates movement of N into surface water because soil erosion by water includes detachment, transport and deposition of soil particles whether through surface flow or raindrops. For example, some sediments may be transported long distance before being deposited or reaching a stream, lake or reservoir. This results in movement of NH_4^+ because it is sorbed to the finer sediments or surface of clays. Meanwhile, NO_3^- is water soluble thus, it moves with water until it re-enters available soil pool, or being utilised by microorganisms, plants, denitrified or deposited to surface or ground water. Mostly, source of N that degrades surface water is that which is transported in soil organic matter [49]. The key factors that influence loss of dissolved N in runoff are soil properties and amount and timing of rainfall. Soil permeability and landscape affect infiltration rate. Soil organic matter, initial water content, soil texture and soil structure influence the amount of water infiltration [49]. Moreover, a combination of high rainfall and soil condition of high runoff potential accelerates surface runoff losses. Incomplete incorporation of surface-crop residues and higher dissolved N concentration in surface soil because of accumulation of residues and decomposition might be the reasons for high surface runoff. Lehman and Ahuja [134] added that when there is barrier such as Fragipan in the soil profile, high concentration of soluble N can occur resulting in return flow of leached N back to the soil surface.

22. Nitrogen Use Efficiency

Lassaletta et al. [135] reported that, the world Nitrogen Use Efficiency (NUE) on agricultural lands has declined by approximately 20%. Nitrogen Use Efficiency has various definitions [136], such as the definition of Nielsen [137], that NUE indicates the relative balance between the amount of fertiliser taken up and used by crop versus the amount of fertiliser N lost. Another definition of NUE is yield per unit of N available in the soil [138]. In addition, NUE can be defined as crop yield per unit of nutrient applied [139]. According to Kant et al. [138], in the plant life cycle, there are two stages for N used. The first stage is during biomass formation when there is amount of N uptake, assimilation into amino acids and nitrogenous compounds and storage. The second stage is the amount of N partitioned to the seed, resulting in final yield. At the plant level, NUE is subjected to N uptake efficiency (NUpE) and N utilisation efficiency (NUtE) [73,79,140,141]. Xu et al. [73] defined NUpE as the capability of plant roots to take N from the soil and NUtE was defined as the fraction of plant-acquired N to be converted to total plant biomass or grain yield. Some NUE calculations take into account only nutrient inputs from fertilisers and nutrients from mineralisation of organic matter, manures and crop residues over several crop cycles [142]. However, it also depends on the form of N taken up and applied [79,141]. The amount of remaining mineral N after harvesting crops plays an important role in the environmental N pollution problem [143] because a high NUE does not suggest N surplus does not surpass critical environmental threshold. The three commonly used as NUE indicators are partial factor productivity for N fertiliser (PFP_N, kg grain kg^{-1} N_{fert}), apparent N use efficiency (ANUE, %) and N recovery efficiency (RE_N, %). The ratio of crop yield per unit of mineral fertiliser N applied is the definition for PFP_N [144,145] and it is calculated as:

$$PFP_N = Y_g / N_{fert} \tag{13}$$

where, Y_g = grain yield (kg ha^{-1}), N_{fert} = amount of N mineral fertiliser application rate (kg N ha^{-1}).

Al Naggar et al. [146], demonstrated ANUE formula as:

$$ANUE = N_g / N_{fert} \tag{14}$$

where, N_g = quantity of N in grain (kg N ha^{-1}), N_{fert} = amount of N mineral fertiliser application rate (kg N ha^{-1}).

The ratio of N output in harvested products to N inputs is the definition for RE_N [147,148] and the formula was as follows:

$$RE_N = N_g / N_{input} \tag{15}$$

where, N_g = quantity of N in grain, N_{input} = total N input.

23. Factors Affecting Nitrogen Use Efficiency

Every genotype has its special functional and morphological characteristics that affect N uptake and the use of absorbed N; thus, species and cultivars are expected as the main factors affecting NUE [149]. However, Burns [150] opined that when subjected to different levels of N availability, the same genotype can show different NUEs. It is the view of Han et al. [151] that besides genetics, there other factors need to be considered such as the interaction between water availability with N uptake, interaction between C metabolism and N utilisation and interaction between macro and micronutrients. In addition, improving NUE depends on factors such as C status, water, soil type, temperature and light as these factors affect N uptake, assimilation and remobilisation efficiency because components of NUE intermingle in numerous and complex ways with other metabolic pathways [138]. Environmental factors such as soil texture, temperature and rainfall affect crop development and growth or the availability of N in the soil through mineralisation of soil organic matter, organic fertilisers and on nitrate leaching [152] thus, affecting NUE. In addition, factors such as environmental regulation changes, water quality concerns and N fertiliser price fluctuations [153,154] partially cause low NUE in corn production [135,155]. Apart from environmental conditions inhibiting microbial activities, potential limiting factors are physical protection of organic matter within soil matrix, complexation with soil minerals, rhizodeposition or alternative source of low molecular weight of C and chemical recalcitrance [156,157]. Achieving synchrony between plant demand and N supply optimally without deficiency or over-supply is the key for optimising trade-offs between yield, income and environment. Thus, agricultural systems need to work within a 'safe operating space' for N use [158] where NUE is neither low that large amounts of reactive N are lost to the environment, nor high that soils are degraded.

24. Ammonium Adsorption and Desorption

Buss et al. [159] reported that the reactive processes controlling subsurface movement for NH_4^+ include sorption causing cation exchange and biological degradation. Charcoal is one of the highly efficient adsorbents to remove excessive application of N fertilisers, organic and inorganic contaminants and heavy metals because of its potential physico-chemical properties such as large internal surface area, well developed porous structure, wide spectrum of surface functional groups, high cation exchange capacity, water holding capacity and low bulk density. In order to understand the adsorption mechanism of charcoal, the nature of the NH_4^+ as an adsorbate should be known. Furthermore, the physical and chemical properties of the organic and inorganic compounds with surface functional groups of the charcoal is needed. Similar to biochar, charcoal adsorbs NH_4^+ via electrostatic exchange with cationic functional groups on the surface of charcoal because of its abundant negatively charged surfaces. Furthermore, the CEC of charcoal is one of the most vital factors affecting NH_4^+ adsorption. Amending soils with charcoal can enhance retention of NH_4^+ in soils because of its high affinity for NH_4^+ sorption compared with soils. However, at low pH values, the NH_4^+ adsorption capacity decreases because at low pH, competition between H^+ and NH_4^+ for the active sites of the charcoal surface increases, resulting in low NH_4^+ adsorption capacity [160]. Conversely, when pH values are higher than 8, the NH_4^+ ions are transformed to NH_3 gas, causing depletion in NH_4^+ adsorption capacity. Therefore, the optimum pH for NH_4^+ adsorption ranges between 5 to 8 [161–163]. The relevance of pH in cation sorption is well established because it affects the chemical speciation of the NH_4^+ in solution as well as the ionisation of chemically active sites on the sorbent. As a result, the net charge of the sorbent surface play an important role in sorption processes, and analysis of protonation-deprotonation behaviour of sorbent materials in aqueous conditions is significant in explaining sorption mechanisms [164]. The pH at which the sorbent surface charge becomes zero is referred to as the point of zero charge (PZC). At this pH, the charge of the positive surface sites is equal to the charge of negative surface sites. The point of zero charge enables to hypothesise on the ionisation of functional groups and their interactions with NH_4^+ in the solution. The pH of the solution is higher than point of zero charge, indicate that the sorbent surface such as charcoal and wood ash are negatively charged enable the interaction between positive ions such as NH_4^+ [164]. Moreover, the knowledge of point of zero charge of charcoal and wood ash provides information about the possible attraction and repulsion between charcoal and wood ash and NH_4^+ ions. However, it also allows to ensure that electrostatic force is one of the mechanisms that occurs in NH_4^+ sorption. Even though Makoto and Koike [165] believe that the adsorption capacity of charcoal affects N dynamics differently because the function of charcoal as adsorbent is relatively short although it has the potential to remain in soils for thousands of years, as its pores become clogged [165]. The adsorption process commonly examined to obtain optimum conditions based on mathematical models are obtained from laboratory results such as pseudo-first order, pseudo-second order and intra-particle diffusion for kinetics studies whereas, Langmuir and Freundlich models are for isothermal studies. Adsorption of wood ash in soils enhances microbial growth to immobilise C in addition to reducing nutrient leaching through improved soil stability. Similar to charcoal, adsorption of NH_4^+ on the surface of the wood ash is influenced by its specific surface area and porosity. Even though charcoal exhibits higher adsorption capacity, ash has a potential as an intermediate adsorption capacity [166]. Gómez-Rey et al. [167] opined that in N limited soils, co-application of wood ash and N fertiliser balances soil N immobilisation.

25. Kinetics of Sorption Model

Özcan et al. [168] described that the kinetics of adsorption is one of the key characteristics defining the efficiency of adsorption because the study of kinetics model establishes important information for the reaction pathways and sorption reaction mechanism [169,170]. Moreover, the kinetics of sorption depends on the physical and chemical characteristics of sorbent and sorbate [169,171,172]. To determine adsorption isotherms, the adsorption kinetics of NH_4^+ need to be studied using three kinetics models such as the pseudo-first order, pseudo-second order kinetic models and intra-particle diffusion model (Table 4) [163,173,174].

Table 4. Kinetic Models of Ammonium Sorption.

Kinetic Models	Equation	Plot	Reference
Pseudo-first order	$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.203}$	$\log(q_e - q_t)$ vs. t	[175]
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e 2} + \frac{t}{q_e}\ v_0 = k_2 \times q_e 2$	$\frac{t}{q_t}$ vs. t	[172,175]
Intra-particle diffusion	$q_t = k_i \times t^{1/2} + c_i$	q_t vs. $t^{0.5}$	[172]

Where: q_e is amount of ions adsorbed per unit mass of the adsorbent at equilibrium time, [mg/g]; q_t is amount of ions adsorbed per unit mass of the adsorbent at time t (mg/g); t is contact time [min]; k_1 is pseudo-first order rate constant [1/min]; k_2 is the pseudo-second order rate constant (g/mg min); k_i is intra-particle diffusion constant (mg/g $\text{min}^{\frac{1}{2}}$); C_i is intercept directly propotional to the thickness of the boundary layer (mg/g) found in [176].

26. Adsorption Isotherm

Yuan et al. [177] defined adsorption isotherm as the relationship between concentration of the solute in the solution and quantity of the adsorbate adsorbed by sorbent in equilibrium at constant temperature. The Langmuir isotherm is based on the assumption that uptake of NH_4^+ occurs by monolayer adsorption without any interference between adsorbed ions on a homogeneous surface [178,179]. This isotherm model represents the equilibrium distribution between solid and liquid phases of NH_4^+ ions. The underlying hypothesis of this model it is for all active adsorption sites with same energy. The linear form of Langmuir equation is reported as [180,181]:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{16}$$

where, C_e (mg/L) is the equilibrium concentration in solution, q_e (mg/g) is the amount of NH_4^+ ion adsorbed at equilibrium. q_m (mg/g) is the maximum NH_4^+ ion uptake per unit mass of the adsorbent, which relates to adsorption capacity. b is the Langmuir constant (L/mg) which relates to the adsorption rate. The q_m and b can be determined from C_e/q_e versus the C_e plot which gives a straight line of slope $1/q_m$ and intercept $1/(bq_m)$.

The essential characteristics of Langmuir adsorption isotherm is described in terms of dimensionless constant known as separation factor or equilibrium parameter as [182]:

$$x = abC/(1 + aC) \tag{17}$$

where, x is the total amount of NH_4^+ adsorbed (mg/kg), a is the constant related to the binding strength (mg/kg), b is a sorption maximum, C is the NH_4^+ concentration remaining in the solution after the equilibrium (mg/kg).

Hui et al. [183] reported that the Freundlich isotherm used to designate the adsorption of inorganic and organic constituents in solution. This Freundlich isotherm model involves heterogeneous sorption and it suits a non-ideal sorption. It describes multilayer adsorption. The isotherm is expressed as follows [179]:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{18}$$

where, C_e is the equilibrium concentration in liquid phase (mg/L), q_e is the maximum amount of NH_4^+ adsorbed at equilibrium [mg/g], K_f is the Freundlich adsorption capacity and $1/n$ is the sorption constant having a value range between 0 and 1.

Another approach isotherm studies is to calculate the partitioning of solution and solid phase known as adsorption-desorption distribution coefficient (Kd). It is also referred to Freundlich solid-water adsorption capacity (K_f). Distribution coefficient is the ratio of concentration in the solid phase to concentration in the solution phase. It is an essential information for understanding the mobility of a compound in the environment and its distribution between water, sludge, soil and sediment. The distribution of a chemical between water and soil, sludge and sediment are determined by the chemical properties as well as the matrix. In agricultural fields, temperature and rainfall affect the distribution coefficient. The low Kd values suggest weak interaction between NH_4 and surface of charcoal [184]. Due to this, the NH_4 ions on the surface of the charcoal and wood ash can easily interchange with other's cationic species.

Brunauer-Emmett-Teller (BET) theory is another well-known approach for characterisation of catalyst, adsorbents and natural or artificial porous materials. This BET is a typical approach for calculating specific surface area by estimating N adsorption isotherms for determining specific surface area [185]. BET theory is related to Langmuir isotherms which were limited to monolayers. BET assumes that adsorbent surfaces are ideally flat and that gas molecules can adsorb on this surface of an adsorbed molecule [186]. Additionally, BET theory assumes that all layers involved in multilayer adsorption are in equilibrium [187]. This phenomenon is stimulated by Van der Waals forces generated by the adsorbate layer which is made up of atoms, ions or molecules on the surface of a charcoal that adsorbs their particles [186]. The amount of the adsorbed N gas on charcoal as adsorbent material can be correlated with its surface area. The BET surface area of charcoal increases with increasing pyrolysis temperature, especially at 500 °C to 700 °C. [188] because, volatiles are rapidly released at high temperature, resulting in the rapid formation of charcoal porous structure. The adsorption energy difference between the first and second layer is linked to the dimension less C parameter.

$$C \approx \exp\left((\mathrm{E}_1 - \mathrm{E}_2)/\mathrm{RT}\right) \tag{19}$$

where, E_1 and E_2 the molar adsorption energy for first and second layer. The adsorption energy of the third and higher layer is equal to the second. In general, it is the quantity of interest since it produces the specific surface area when multiplied by the cross-sectional area of the sorbate. The BET equation is expressed as follows [189]:

$$((P/P_0)/n\,(1 - P/P_0)) = (1/n_m\,\mathrm{C}) + ((c - 1)/(n_m\,\mathrm{C}))\,(P/P_0) \tag{20}$$

where, P is the pressure, P_0 is the saturation pressure of a substance being adsorbed at the adsorption temperature, n is the specific amount of adsorbed gas at the relative pressure P/P_0, n_m is the monolayer capacity of the adsorbed gas, C is the BET constant which is exponentially related to the energy of monolayer adsorption. The shape of an isotherms in the BET range obtained from parameter C. When the maxima arrangement approach is used, the values of C are positive, this avoids erroneous n_m evaluation from occurring when an improper pressure range is used to construct a BET plot [186]. However, because this approach is based on gas adsorption, limitations are commonly associated with monolayers. For example, the validity of BET monolayer capacity (n_m) is problematic. Moreover, the monolayer structure is not the same on all the surfaces especially when N_2 isotherms are used. Additionally, according to the International Union of Pure and Applied Chemistry (IUPAC), wood charcoal exhibits type 1 N_2 adsorption isotherm and H 4 hysteresis loop representing narrow slit pores in the microspores region (Average pore radius < 50 Å) [190]. Based on the BET theory that significant overlap between monolayer and multilayer coverage would undermine the assumption that adsorption occurs via formation of multilayer [191]. Mel'gunov and Ayupov [186] believe that if the value of cross-sectional molecular area is known, the BET surface area analysis theory could be applied for any adsorbates and adsorbents at any temperature. It is the view of Van Erp and Martens [185] that reproducibility issues develop because of a systematic divergence between BET theory and the actual experimental condition, in which the hypothesised assumptions are not completely achieved.

27. Types of Spectroscopy

X-ray absorption spectroscopy (XAS) consists of extended x-ray absorption fine structure (EXAFS). X-ray absorption spectroscopy measures the x-ray absorption coefficient of a material as a function of energy. Each element has a unique set of absorption edges that correspond to the different binding energies of its electron, resulting in XAS element selectivity. Extended x-ray absorption fine structure, being a very sensitive technique, is a convenient tool to determine the chemical state of species that may exist even at very low concentrations. Synchrotron-based X-ray absorption fine structure spectroscopy has been reported as a powerful tool for elucidation of metal speciation in soils treated with soil amendments [192]. Energy dispersive EXAFS aids in the determination of structural and kinetic characteristics in supported metal catalysts for reactions that occur on a timescale of a few seconds [164]. X-ray photoelectron spectroscopy (XPS) is one of the standard tools for surface characterisation. The XPS analysis is performed to identify the elemental composition such as carbon, oxygen and nitrogen, types of acidic functional groups and their relative percentage on the surface of charcoal. The formation of surface oxygen on charcoal enhances the oxygen containing complexes to improve ion exchange properties during adsorption. However, it should be noted that XPS analysis estimates the structure to a few nanometers in depth [193].

Fourier transform infrared spectroscopy (FTIR) is one of the techniques that determines the structure, composition and size of nanoparticles. It is a technique for measuring the absorption of electromagnetic radiation with wavelengths in the mid-infrared range (4000–400 cm^{-1}) [164]. In general, charcoal is composed of C atoms, and heteroatoms such as O, H, N, and S. As a result, several functional groups dominate the surface of the charcoal and FTIR provides information on these chemical structures [194]. The presence of more acidic functional groups on the surface of the charcoal promotes cation adsorption such as NH_4^+ during chemisorption process [193]. The most prominent bands representing functional groups on the surface of charcoal are ≈3500, 1700, 1610, 1420, and 1140 cm^{-1} indicating free or intermolecular bonded OH groups, carbonyl (C=O) stretching vibrations of carboxyl groups, ketones or aldehydes, C=C double bonds aromatic rings, and ether C–O stretching bonds, respectively [194]. Charcoal demonstrates OH, –CH and C=O stretching in the regions of 3500, 2926 and 2858 cm^{-1} [195]. In addition, well distinguished peaks are observed near 1100 and 780 cm^{-1} and they represent OH bending and $=CH_2$ bands [196]. The point of zero charge values for charcoal range from 7.4 to 9.9 [191]. Thus, at normal pH (6 to 7), charcoal is protonated, to sorb anionic contaminants via electrostatic interaction [197].

28. Ashes and Their Chemical Composition

Wood ash is considered as significant source of mineral, a product of incomplete combustion of wood containing inorganic and organic compounds [198] such as mixtures of oxides, carbonates, hydroxides, silicates and its N is low because N aquires volatilised during combustion [199]. Ash can be utilised as an alternative chemical fertiliser that can act as a liming agent to improve nutrient cycling because of its high solubility and availability of macronutrients for plants. The relative amounts of the major nutrients in ash are in the order of $K > Mg > Ca > P$ [200]. These nutrients are important in the formation of nucleotides, phosphatides, chlorophyll and alkaloids, synthesising enzymes, vitamins and hormones [201]. Pitman [202] stated that depending on growth conditions, different wood have several amounts of mineral compounds. For example, hardwood ash has a lesser amount of Ca and Si but is higher in K and P than softwood ash.

29. Properties of Ashes

The properties of ash differ depending on the amount of bark burned, species of the plant, growth conditions and contamination of materials from harvest operation such as soil [203]. The temperature during combustion is also important. For example, temperature below 500 °C produces carbonates and bicarbonates whereas at or above 1000 °C, the most prevalent compounds are oxides and hydroxides [204].

30. Use of Ashes in Agriculture

According to Van Laer et al. [32], wood ash has been utilised as a soil conditioner. Wood ash which is produced through combustion is not only alkaline but it also high in soluble macronutrients such as Ca, K, P and Mg [33]. Moreover, wood ash has a potential to reduce nutrient loss from crop harvesting and it is also ideal for acid soils that are highly weathered because of the acid neutralising capacity of wood ash. When soil acidity decreases, base saturation and microbial activity increase [34]. However, with time, the ash as soil amendment reduces because of biogeochemical interactions between amendment and soil profile [35,36]. The adsorption properties of wood ash are influenced by its specific surface area. This can also be associated with the pore size that affects the type of molecules that can be adsorbed on the surface, wood ash and C residues with larger surface area increased the adsorption properties [37]. Moreover, wood ash can increase water holding capacity, moisture content and nutrient availability because its hydrophilic property enhances soil water retention [38], microbial activities [205,206], improve growth and crop yields [207–209] and availability of P, K, and B. Over utilisation of wood ash could damage plants because it contains some toxic substances such as Caesium-137 as radioactive elements and some elements such as As, Pb, Zn, Ni, Co, and Cu which can be toxic to plants and cause environmental problems [210]. These toxic substances can disturb nutrient cycling in soils and microbiological processes if excess wood ash is applied which adversely affect plant growth [198,211]. Nabeela et al. [198] reported that application of wood ash resulted in increase in bioaccumulation of trace elements in *Brassica napus* L. seedlings and the order of bioaccumulation was Fe > Zn > Pb > Co > Cu > Cd > Ni.

31. Mechanism of Bark Ash on the pH of Tropical Acid Soils

Augusto et al. [212] reported that, different oxides formed during combustion and consequent aeration can cause formation of carbonates in ash, making the ash alkaline (pH 8 to 13). Moreover, utilisation of ash as soil amendment can return essential nutrients back to the soil apart from neutralising soil acidity. The rapid changes in pH are influenced by carbonates, oxides, hydroxides and hydrogen carbonates. Addition of ash does not only increase soil pH but it also indirectly stimulates microbial activities [213] which play an important role in decomposition and mineralisation. The use of wood ash caused rapid changes in the chemical properties of the soil particularly the topsoil [214]. Arvidsson et al. [215] revealed that, the neutralising effects of wood ash are very minimal or none in the deeper layers.

32. Charcoal

Charcoal is a solid carbonaceous residue which is produced by heating through slow and rapid pyrolysis, gasification and hydrothermal carbonisation under oxygen-deficient conditions [15]. Charcoal is produced through slow pyrolysis [16] and it is highly resistant to decomposition [17,18]. Charcoal in soils has been well recognised to influence the nature of sorption mechanism and improves sorption of organic pollutant [19,20]. Charcoal can positively impact on soil processes and properties for the first few decades after its formation [17,21,22]. In carbonaceous materials, adsorption is regulated by physical and chemical structures [20].

Adsorption is commonly used as an efficient physical separation mechanism to remove or reduce the concentration of a diverse variety of dissolved contaminants whether organic or inorganic pollutants [23]. Charcoal structure reflects the morphology of its raw material [24]. A typical charcoal consists of C, H, N, S, ash, and oxygen [25]. In addition, its structure, composition and characteristics such as particle size distribution, moisture content, density, ash content and pH depend on the form, nature and origin of raw material, in addition to the state of thermal conversion cycle [26]. Furthermore, C materials are resistant to toxic conditions and corrosive environments such as basic and acidic conditions. The utilisation of C as the material is due to its special structure and electrical conductivity [31]. Factors that affect the properties of charcoal are the form of organic matter used, the charring environment and additions during the charring process. The source of charcoal material has significant impact on the direct effects of the alteration of charcoal amendments on nutrient contents and availability. Moreover, microbes have significant impact on the properties of charcoal [30] because surface oxidation is the most significant coal weathering mechanism contributing to an increase in functional groups such as carboxyl and carbonyl at the exchange sites [216]. Losses of charcoal from soil occur in different ways such as erosion by surface runoff [30,217,218], biotic, and abiotic degradation [30]. In addition, alteration of charcoal physical, chemical and biological properties can occur because of environmental exposure and this cause long terms changes in its hydrological, microbial and nutrient retention services [21,219,220]. Multiple processes including chemical and physical weathering [221], infilling pores with soil-mineral or soil-humic substances [222] and biological alteration [222–224] can significantly alter the density and porosity of charcoal after being introduced to the environment.

33. Charcoal Porosity

Depending on its raw material and production temperature, charcoal is highly porous with approximately 55 to 85% total pore volume. The pore size ranges between subnanometers and tens of micrometers [225,226]. Charcoal pores are divided into macro-pores, meso-pores and nano-pores [227]. Approximately 95% of charcoal's total porosity is dominated by macro pores with >50 nm in size, that are important as microbial habitats and water retention. Meso-pores (2–50 nm) and nano pores (<2 nm) are essential for nutrient retention and charcoal's active surface area represent approximately less than 5% of its total porosity [225,226,228] (Figure 1). Trubetskaya [229] opined that charcoal from hardwood species is less porous than softwood leading to its lower reactivity at high temperature pyrolysis. The distribution of pore size and porosity of charcoal also influence its hydrological and ecological capabilities in soils [230–232]. The distribution of the pores is significant as an ecological niche for soil microbes because micron-sized pores are abundant in biomass-derived charcoal, and inherited from cellular plants, are suitable for soil microbes such as most bacteria and fungi [226,233]. A charcoal with high volumes of pores can increase soil total porosity and water holding capacity. Several pore sizes distribution enhance retention of plant available water [232]. In most literature, adsorption takes place in micropores, nevertheless macropores and mesopores contribute as a passage for the absorbate to the micropores, because only a small number of the pores are on the outer surface of the charcoal.

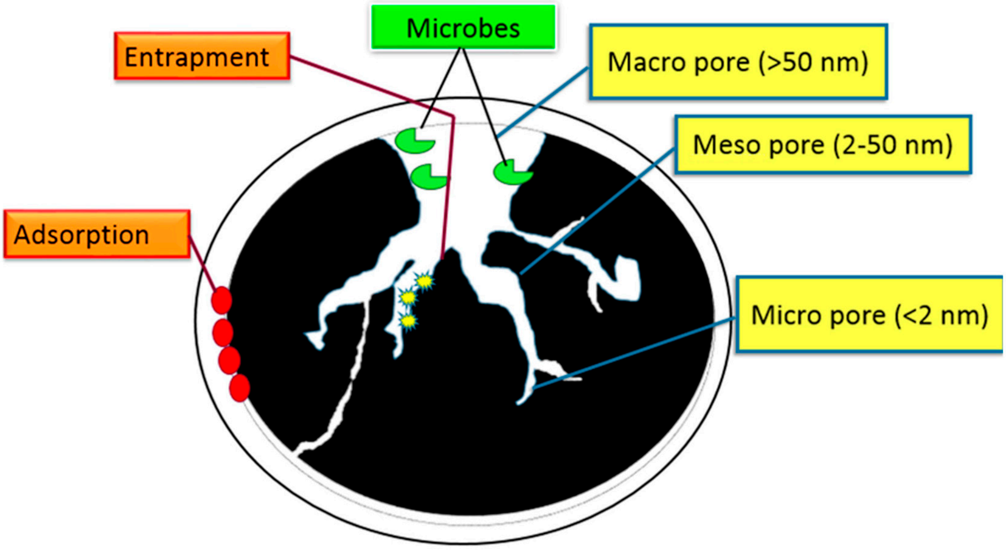

Figure 1. Illustration of pore distribution [227].

34. Charcoal as an Amendment That Retains Nutrients in Agriculture

In arid and humus-poor areas in particular, charcoal can significantly improve soils in these regions because it is resilient in soil, thus it decomposes slowly over the long term [25]. Hermann et al. [234] reported that, approximately 50 to 80% of charcoal C is integrated in soil system. Previous studies demonstrated that charcoal has some soluble iron oxides to increase soil pH. This is important for plant growth because it improves soil fertility, besides reducing soil tensile strength to facilitate root growth and root predation, and enabling seeds germination [235–237]. Charcoal has different inorganic and organic forms of N and P such as NO_3^-, NH_4^+, amide groups and ortho-P [27,28]. However, the concentrations of these nutrients depend on the production temperature and its sources. For example, charcoals produced at lower temperature have more $NH_4{}^+$, whereas charcoals produced at higher temperature tend to be high in $NO_3{}^-$, and charcoal produced from plant residues usually have higher nutrient content than charcoal generated from ligno-cellulosic feedstocks [29]. Not only the contents of nutrients, but also the conservation of nutrients can be enhanced by applying charcoal to soils. This is particularly relevant in heavily weathered soils with poor ion retention ability [30]. Moreover, charcoal has high-specific surface area because of its porous structure, surface electrostatic properties [236,238] and rich in high concentration mineral nutrients present after formation on its surfaces [29,239,240]. These properties enable charcoal to alter nutrient accessibility through inputs of the nutrient it is contain [30,241], increases pH and soil water holding capacity [22,242,243], promote microbial activity and nutrient fluxes [29,236,244] and increase sorption of secondary compound that impede soil processes such as phenolics [21,245]. Furthermore, addition of charcoal to soils enhances seed germination, plant growth and yields particularly in the tropics [30]. Added charcoal not only act as soil conditioner but also acts as an amendment to increase CEC, reduce the Al saturation of acid soils, and improve free bases availability such as Ca, K and Mg [30]. However, excessive addition of charcoal or coal derived humic acids can have adverse effects on crop production [30].

35. Nutrient Sorption Mechanism of Charcoal

Charcoal as an amendment has influences the diversity and composition of soil microbial communities [246–248] by altering the soil microclimate such as pH, water holding capacity, bulk density, cation exchange capacity and structure of the soil [249–251]. Makoto and Koike, [165] revealed that charcoal influences saprotrophic microbes. In addition, charcoal provides nutrient and source of C directly and indirectly to microbes because of its high surface area. Its ability to adsorb nutrient making it available for microbe’s consumption [19,252,253]. The large surface area and porosity of charcoal provide habitat for soil microbes from soil predators [35,254]. It can remain in the soil ecosystem for hundreds to thousands of years because its aromatic structure is highly recalcitrant to soil microbial decomposition [249]. However, Khodadad et al. [247] opined that alteration of the soil microbial community stimulated by charcoal differ according to soil type and the raw materials from which the charcoal was produced. Makoto et al. [255] reported that charcoal buried in subsurface soil had a positive effect on seedling growth and rhizosphere compare with charcoal deposited on the soil surface. Moreover, there are several major ion sorption mechanisms onto charcoal such as surface precipitation, chemical reaction with surface functional groups, entrapment in the solution into interior pores and electrostatic adsorption [256,257]. Gierak and Lazarska [258] reported that the adsorption of ions does not only depend on specific surface area of charcoal as an adsorbent, but presence of the surface groups is also important. This is because the oxidation of active C increases amount of oxygen functional groups on the surface of charcoals, which results in an increase in polarity and hydrophilicity of the surface of charcoals. Content and the nature of the emerging oxygen functional groups [259,260] affects the conditions applicable during modification of C as well as applied oxidisers. The surface functional groups include carboxyl, carbonyl, phenol, quinone, lactone and other groups bound to the edge of graphite-like layers enable the complex formation between the adsorbed molecule and the carbonyl group of the charcoal which makes it suitable as adsorbents. In addition, Jankowska et al. [261] stated that the C material which is oxidised in the liquid phase or chemically oxidised in the gas phase within a range of 300 °C to 500 °C can exchange cations.

36. Water Retention Mechanism of Charcoal

Similar to biochar, addition of charcoal to soils can have direct and indirect effects on soil water retention. The direct effect is due to the porosity of charcoal and high internal surface area where the retention of water occurs by capillarity. Overall, this can improve soil water content, porosity, in addition to reducing mobility of water, thus reducing water stress in plants. Improvement in soil structure and aggregation are the indirect effects of water retention in soil influenced by charcoal [238,260].

37. Nitrate Retention Mechanism by Charcoal

Nitrate is negatively charge, highly soluble in water and it moves with soil water. Commonly, soils are unable to adsorb nitrate because at their natural pH, anion exchange capacity is insufficient. Due to its negative charge, NO_3^- is repelled by the negatively charge soil colloids. With the aid of charcoal's unique pore structure, soil water is trapped inside charcoal pores and NO_3^- remain in available formed until they are taken up by plant. Figures 2 and 3 demonstrate the mechanisms of how charcoal prevents leaching of NO_3^- in soil water during heavy rainfall. However, the role of charcoal in retaining NO_3^- depends on its adsorption capacity such as raw material used and temperature for pyrolysis [105].

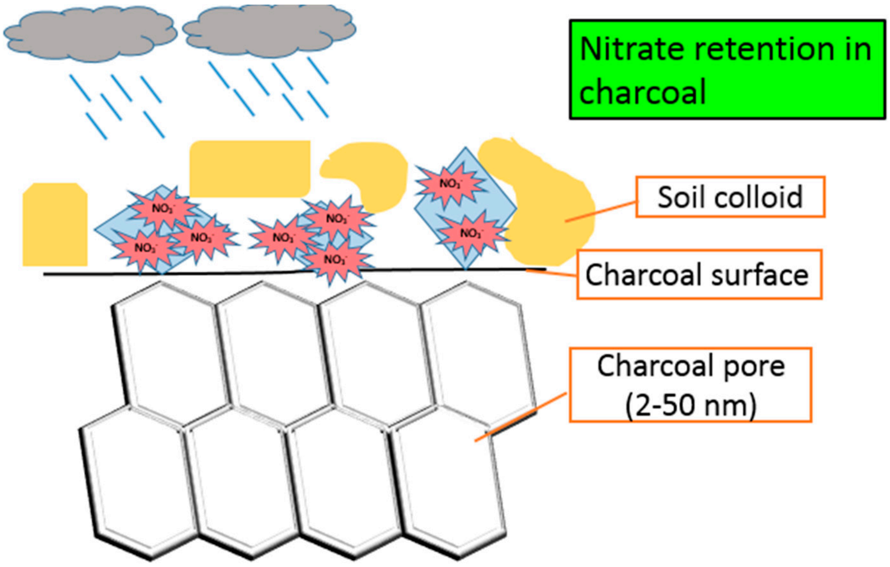

Figure 2. Schematic illustration of the process of leaching with charcoal.

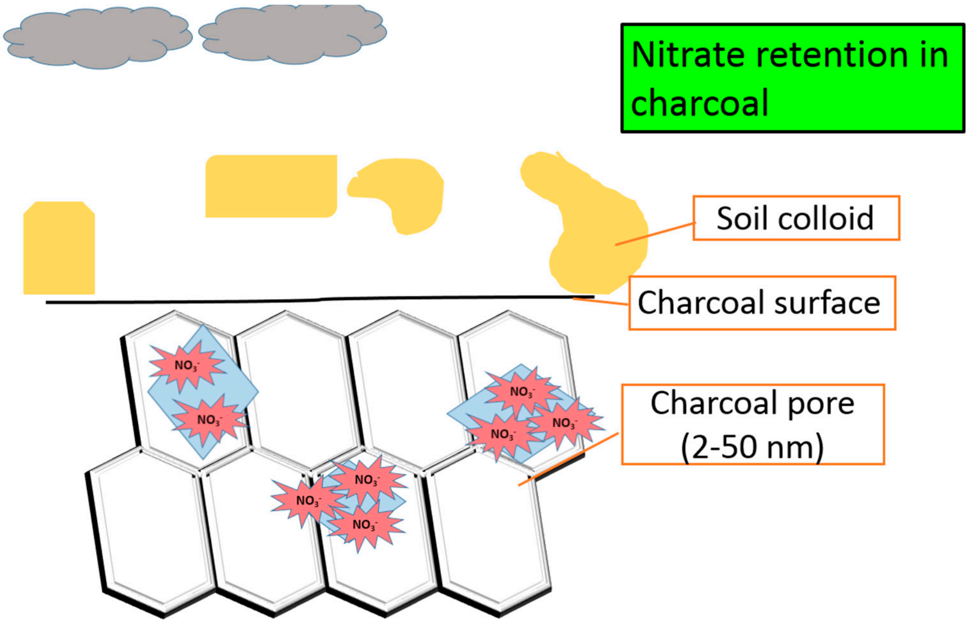

Figure 3. Schematic illustration of the entrapment of nitrate in soil water inside charcoal pores.

38. Ammonium Retention Mechanism by Charcoal

Similar to biochar, charcoal's capacity to sorb NH_4^+ ions is because of its physical and chemical properties. Charcoal is an amendment with high-specific surface area and high in CEC because of its porous structure, surface electrostatic properties [238] and rich in high concentration mineral nutrients present after formation on its surfaces [29,239,240]. These properties enable charcoal to alter nutrient accessibility such as retaining NH_4^+ ions through inputs of the nutrient it contains [30,241]. The combination of ash and charcoal as amendments will increase soil pH and enhance NH_4^+ retention at charcoal surface area. Increase in pH will cause dissociation of H^+ from hydroxyl and carboxylate groups, which provide negatively charged surface adsorption sites enables NH_4^+ ions to be retained and remain in its available form. This NH_4^+ retention process is also called NH_4^+ adsorption in which NH_4^+ ions are attached to negatively charged surface that can improve nitrogen availability by remain available to crops and being protected from losses due to leaching.

39. Adverse Effect of Charcoal as Soil Amendment

Pyrolysis of biomass to produce charcoal does not only pledge benefits but it also has its adverse effect. Freddo et al. [262] reported that one of the adverse effects of using charcoal as soil amendment is its possible contamination with organic and inorganic contaminants such as heavy metals and polycyclic aromatic hydrocarbons (PAH). The pyrolysis technologies can increase the concentration of potential pollutants from raw materials because of mass losses [263,264]. In addition, Chen et al. [265] stated that the content of contaminant such as heavy metals increase with increasing temperature of pyrolysis. For example, Keiluweit et al. [266] informed that at 500 °C pyrolysis temperature produced maximum amount of PAH in charcoal. Lyu et al. [267] opined that PAH were produced mostly at 300 °C to 400 °C. Particulate matter and black C can be emitted during pyrolysis, especially on low technology conditions compared with modern pyrolysis plants with high standard filtration technology. Apart from different types of dioxins found produced at 250 °C to 900 °C [268]. Therefore, Shackley et al. [269] suggested health safety and environmental protection when designing the charcoal pyrolysis production technology considering the location of pyrolysis facilities. According to Mohammadi et al. [270] the impact of the toxicities impacted human health is higher particularly when the charcoal is produced in brick kiln, where pyrolysis gases released to the air and not captured.

The addition of charcoal to soils has an inhibitory effect on soil aging. Anyanwu et al. [271] reported that addition of charcoal as soil amendment has negative impacts on earthworms and fungi growth that indirectly leads to reduction of root biomass. This is because decomposition of organic matter has potential to be disturbed by the addition of charcoal as amendment, thus inhibiting fungi growth such as Ascomycota and Basidiomycota by 11% and 66%, respectively [272]. Several studies reported that weed problem arise with the application of charcoal [273].

40. Humic Substances

Humic substances are one of the most important soil components because they form an enormous fractions of soil organic matter in agricultural soils [274]. Based on their solubility in water with various pH values, humic substances can be classified into three fractions namely humic acids, fulvic acids and humins [274]. Chang et al. [275] revealed that humic acids are insoluble at acidic pH but soluble in basic pH whereas humins exhibit low solubility at different pH levels. The formation of humic substances in ecosystems cause formation of oxygen functional groups such as carboxylic, phenolic, alcoholic and carbonyl [276].

41. Humic Acids

Humic acids are organic substances formed from transformation and decomposition of animal, and plant residues through microbial and geochemical activities [277]. Humic acids have a complex surface structure, large specific surface area and abundant functional groups, resulting in having strong adsorption ability [278]. Previous studies reported that humic acids promote improves soil aggregate stability [279], root growth [280], soil N and P availability [281,282] and crop yield. Humic and fulvic fractions have high capacity for metal binding because of their reactive groups such as carboxyl and phenolic groups [283].

42. Fulvic Acids

Fulvic acids are known as complex hybrid of organic micro molecules and polymers including weak aliphatic and aromatic organic acids with significant variability of particle structure and composition [284,285]. Fulvic acids consist of aromatic rings with a range of three to five substituents such as hydroxyl, methoxyl, carboxylic groups, sugars, amino acids and aliphatic hydrocarbon groups with some aldehyde and keto functional groups attached to some of the aromatic nuclei [286–288]. The molecular size of fulvic acids ranges from few hundred to thousands atomic units [284,288]. In soil systems, the physical and chemical performances of fulvic acids are restricted by factors such as pH, temperature, salinity, climates, plant species and microbial activities and populations. Moreover, their composition depends on plant species which provide the initial material for mineralisation and humification, whereas the formation of fulvic acids is influenced by microbial activities [285,288]. In their solid state fulvic acids can attract each other, exhibit highly electrostatically stable charges and can decompose upon heating without burning through gradual charring process. At 50 °C irreversible changes occur [288].

43. Humin

Approximately 50 to 70% of the total humic substances on earth is humin [289]. Lehmann and Kleber [290] opined that humins serve as important component in the natural C cycle through decomposition and CO_2 production. Humins are highly resistant to microbial degradation because it is believed that they are the last residual organic matter produced during humification. Humins have large surface area, making it potential adsorbent with numerous functional groups such as esters, polar aromatic groups and methoxy alkanes [291]. Li et al. [292] reported that bacteria community can affect the structure and types of humin precursors.

44. Changes of Carbon to Nitrogen

The chemical forms of organic matter added and subsequent form can affect the long term soil C and N sequestration efficiency [293]. Wang et al. [294] revealed that soil C is the principal energy source to soil microorganisms and enzymes whereas the soil C/N ratio influences their activity. Soil C and N chemical fractions are theorised to correlate with their half-life and stability. Stable organic compounds can be isolated through hydrolysis of soil organic matter with strong acid [295,296] by producing labile proteins, nucleic acids and polysaccharides, whereas leaving non-hydrolysable long-chain aliphatics and aromatics [297,298]. The non-hydrolysable C and soil humin fractions are correlated to determine the oldest C fractions with radiocarbon dating [299,300]. Plante et al. [296] stated that, the non-hydrolysable C was more associated with silt compared with clay soil particles. Changes in soil enzymes, could also reflect changes in soil C and N which play vital role in soil C and N cycling [301].

45. Current Challenges in Using Charcoal and Wood Ash as Adsorbents

Charcoal and wood ash have been used as adsorbent materials some years ago and claimed to have advantages because of their low cost and suitable to remove heavy metals, organic and inorganic contaminants because of their potential physicochemical properties. Therefore, extensive studies have been carried out. However, there are challenges that limit the practical and large-scale use of charcoal and wood ash as adsorbents. First, in the field of C adsorbents, the stability of the charcoal and wood ash as adsorbents is not fully established. Nevertheless, high adsorption capacity and long-term cyclic operation are also important to ensure the economic viability of using them as adsorbents. For example, wood-based charcoal is cheaper than other adsorbents and can be sufficient adsorbent for some application, however, the characterisation of charcoal is necessary to evaluate its applicability as adsorbent as its depends on the raw material used. The initial capacity of a charcoal can be enhanced to become an activated charcoal after various treatments to enhance the surface adsorption affinity and selectivity towards targeted compounds. However, any modification comes with extra costs. Secondly, physical and chemical modification of charcoal and wood ash have been proposed mostly on laboratory scale. Large scale charcoal use is remains unclear. Moreover, laboratory scale use is mostly explorative. The practical optimisation for large-scale application of charcoal and wood ash as adsorbents are still lacking. This is because most adsorbents used especially for NH_4^+ retention are used are limited laboratory-scale because of the limited availability of both charcoal and wood ash in nature.

46. Conclusions

The proper application and better understanding of the role of charcoal and wood ash as soil amendments could improve soil fertility, N availability, and crop productivity because of their specific physicochemical properties. The high specific surface area and internal porous structure of charcoal increase sorption of NH_4^+ ions and retention of nitrate ions in soil water solution through entrapment inside the pores of charcoal, thus enhancing N availability for plant uptake. Even though adsorption of NH_4^+ ions on wood ash exhibits intermediate adsorption capacity compare with charcoal, it has the potential to reduce nutrient loss besides being ideal for highly weathered acidic soil because of its acid neutralising properties. Sorption isotherms are practical approaches to elucidate retention of N with amendments such as charcoal and wood ash. This is important for understanding the movement of N in the environment. The major advantage of Langmuir equation over Freundlich equation is that an adsorption maximum can be related to several soil properties including, information on the reaction between soil and N fertilisers. Understanding adsorption-desorption distribution coefficient is essential because this approach provides insight on the mobility of a compound in the environment and its distribution between water, sludge, soil and sediment. BET theory is the extended approach to Langmuir isotherm that assumes multilayer adsorption of gas on the adsorbent's surface and all layers involved are in equilibrium. However, this approach is based on gas adsorption, thus the validity of monolayer capacity is problematic. Furthermore, on all surfaces, the monolayer is not the same. The use of charcoal and wood ash could be a better approach in adsorbing N to avoid leaching to maximise nutrient use efficiency. To this end, this review revealed the potential of charcoal and wood ash as soil amendments for agricultural systems because both amendments are highly available and accessible worldwide. In terms of agronomic efficiency, the application method is easy and does not require any special skills or techniques, thus the adoption of the amendments by farmers could be high. For economic and environmental efficiencies, using charcoal and wood ash in farming systems is low in cost because they have been transformed into soil conditioners that are able to improve soil productivity apart from their original materials having the potential of polluting the environment. Greenhouse and field trials are in progress to establish the effects of the combined use of charcoal, wood ash and urea on N sorption in soils.

Author Contributions: Writing—original draft preparation, conceptualisation, visualisation N.H.H.; validation, writing—review and editing, supervision, funding acquisition, O.H.A.; editing second draft L.O. and H.Y.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Ministry of Higher Education, Malaysia with grant number [ERGS/1/11/STWN/UPM/02/65].

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available within the article.

Acknowledgments: The authors acknowledge Ministry of Higher Education, Malaysia for financial assistance [ERGS/1/11/STWN/UPM/02/65] and Universiti Putra Malaysia for providing research facilities.

Conflicts of Interest: The authors declare that there are no conflict of interest regarding the publication of this paper.

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