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Biomass Valorization: Agricultural Waste in Environmental Protection, Phytomedicine and Biofuel Production

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Additional information is available at the end of the chapter

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Abstract

Industrialization is a major promoter of any nation’s economy; it is not without detrimental effects on our immediate environment. Human exposure to various pollutants discharged into the environment may lead to serious health challenges. In the same vein, discharge from the combustion of fossil fuel contributes a great deal to the environmental pollution. The resulting quest for a clean and sustainable environment has spurred myriads of research into advantageous utilization of waste biomass in industrial wastewater treatment and environmentally friendly/alternative energy. Similarly, diverse waste materials have been adopted as sources of important phytochemicals with different medicinal applications. This chapter focuses on the application of waste biomass in environmental remediation, curative medicine, and clean/alternative energy.

Keywords: waste, biomass, bioadsorption, phytochemicals, bioethanol

1. Introduction

Huge amounts of wastes generated during various agro-processes over time constitutes nuisance to the environment. Agro-wastes are cellulosic materials and depending on their sources, may possess high fixed carbon content, multifunctional group surface, and bioactive agents. These characteristics have been well explored and have led to their applications in environmental remediation, phytomedicine, and biofuel generation [1–3].

Biosorption, a sorption technique that utilizes biomass in sequestering various toxicants, is an attractive technique in wastewater treatment. It adds economic advantages to the operational...
simplicity and ability to remove very low concentration of toxicants offered by commercial activated carbon. Surface tailoring toward a specific pollutant is another unique advantage of biomass [4]. Multifunctional group surface and cellulosic backbone of biomass present them as suitable materials for pollutants uptake. Modification and surface treatment may enhance the sorption efficiency of raw biomass [5].

Similarly, waste biomasses have been explored for the beneficial phytochemicals, which they contain. These phytochemicals have been useful as antimicrobials, antioxidants, hepatoprotectives, and anticancer agents, which are generally preferred because of their minimal side effects on their consumers [1, 6]. Obtaining these useful phytochemicals from waste biomass is a very useful and timely development since threat to food security usually results whenever useful compounds of medicinal interest are identified in major food sources [7].

In the same vein, the use of agricultural waste in biofuel production has brought about provision of alternative energy and reduction in environmental pollution. The use of renewable resources such as cornstarch leads to competition with human food supply. In view of this, there is a drift in the use of agricultural waste for biofuel production [8]. Agro-wastes are lignocellulosic materials; their rich cellulose content qualifies them as feedstock in bioethanol production.

This chapter is aimed at explicitly depicting the potential of agricultural wastes in environmental remediation, curative medicine, and biofuel production with focus on research efforts, successes, and gaps.

1.1. Effective wastewater treatment: panacea to water pollution challenges

The advent of industrialization in developed economy brought to bear great environmental pollution challenges. The discharge of toxic wastewater and polluting gases increased exponentially with industrialization and economy [9]. The hydrosphere continuously receives wastewater with loads of toxicants. The effects of such discharge on the aquatic organism and aquatic ecosystem and by extension on human are enormous. Wastewater contains different categories of pollutants ranging from organics to inorganics. Organic pollutants such as dyes form a major part of wastewater discharged from dye-utilizing industries such as leather, textile, and paint industries.

Dyes are large organic molecules, which are nonbiodegradable and carcinogenic; they cause skin, eye, and respiratory tract irritations as well as the reduction of dissolved oxygen and the hindrance of sunlight penetration into water bodies [5]. Heavy metals, on the other hand, are inorganic pollutants with serious deleterious effects on plants and human [10, 11]. Effective treatment of wastewater containing the aforementioned toxicants before their discharge into the environment is thus very important.

Conventional methods of wastewater treatment exist, namely electrochemical treatment, ion exchange, precipitation, reverse osmosis, evaporation, solvent extraction, adsorption with activated charcoal, among others. Disadvantages associated with conventional methods of wastewater treatment may be a concern to the developed and the developing economy. For instance, toxic sludge generation in chemical precipitation subsequently results in soil and
water pollution. Inability of conventional methods to remove low concentration of pollutants also calls for concern. In addition, cost of installation, operation, and maintenance is a great concern to developing economies. Adsorption using activated charcoal is a way out of some of these earlier mentioned challenges. However, activated charcoal is very expensive.

Naturally occurring low-cost adsorbents/biosorbents, such as clay and agricultural wastes, particularly, crop residues, may effectively address the challenges associated with conventional methods of wastewater treatment. Due to the basic composition of crop residues, they have been widely investigated as a potential tool for effective wastewater treatment.

1.1.1. Crop residues as a tool in environmental remediation: characteristics, uniqueness and versatility

Crop residues are the part of crop production processes not used as food for human. They are not the primary products usually consumed as food. These may come in the form of stalks, straw, leaves, roots, peels, husks, cobs, shells, nuts, and even waste woods. The composition of these crop residues may vary depending on their sources [12]. However, they are characterized by similar features and basic composition.

1.1.1.1. Polyols backbones

The basic components of crop residues are cellulose, hemicellulose, lignin, and some extractives [13]. While cellulose is a crystalline $\alpha$, $\beta$ (1–4) linked D-glucose polymer with high molecular weight, hemicellulose is an amorphous, shorter chain polymer of various sugars. These two components (cellulose and hemicellulose) contain numerous hydroxyl groups and thus result in a characteristic polyols backbone in crop residues. The polyols surface presents suitable sites for the uptake of pollutants. The deprotonation of hydroxyl group leaves on the residue surface a number of electron-rich oxygen atoms. These electron-rich species could act as Lewis bases, thus attracting electron-deficient species such as metal ions as depicted in Figure 1.

1.1.1.2. Multifunctional group surface

Aside the basic hydroxyl groups present in these crop residues, their surfaces may also carry other functional groups such as carbonyl, carboxyl, methoxyl, sulphhydryl, ether, acetamido, or amino groups. These functional groups, however, may vary depending on the crop residue source, variety, age, and environmental and cultivation parameters [14–16]. Common to these functional groups is the possession of lone pairs with which they chelate (bite) metal ions. Metal and dye sequestering by different parts of the residue can occur via various processes among which are the following:

Complexation: A process in which metal ions form complexes with organic molecules. This organic species must have an atom or atoms having lone pair of electrons to donate.

Chelation: A process in which organic molecules containing more than one functional group with donor electron pairs simultaneously donate these to a metal atom resulting in the formation of a ring structure involving the metal atom. Due to the multiple binding sites, chelates are more stable than complexes.
Precipitation: Precipitation is a double decomposition reaction in which toxic metal ions are removed from solutions. This has been used severally in biosorption.

Reduction: Reduction is a process involving electron gain. Removal of toxic hexavalent chromium from aqueous solution by biosorption has been reported, and it is often associated with the simultaneous reduction of \( \text{Cr} \ (\text{VI}) \) to \( \text{Cr} \ (\text{III}) \).

Immobilization may be the result of more than one mechanism; for example, metal complexation may be followed by metal reduction or metal precipitation.

The high binding ability of the aforementioned functional groups with a wide range of pollutants via various mechanisms presents crop residues as excellent tools in environmental remediation.

1.1.1.3. Fibrous nature and possible porosity

The characteristics of crop residue are well understood and established by studying their surface morphology and porosity. While some crop residue depicts vivid threadlike surface
fibers, pores scarcely appear in some, and some others may possess naturally wide-open pores and hollows. Fibrous character is synonymous with wood waste [17], and a range of water pollutants can be locked up within the crop residue fibers. Pores and hollows also serve as mediums for transporting various types of pollutants into the bioadsorbents. Mesopores (pores with size range between 2 and 50 μm) are more useful in the transport and trapping of large molecules such as dyes into the bioadsorbents [4]. Scanning electron microscopy studies (SEM) of two biomass (Irvingia gabonensis nut and Raphia hookerie epicarp) as investigated by Inyinbor and colleagues reveal the fibrous nature of I. gabonensis biomass, while several moderately large pores were observed in R. hookerie biomass (Figure 2a and b).

1.1.1.4. Carbon content and versatility

Crop residues are generally characterized by high carbon content. Hence, they have found great application in diverse fields. Their use in environmental remediation spans through utilizing raw bioadsorbents, modified biomass, as well as biomass-generated activated carbon for pollutant uptake. The high fixed-carbon content in raw biomass significantly aids pollutant uptake [18].

Pollutants may be chemisorbed via its interactions with surface functional group(s), locked in the fibers, or trapped within the biomass pores. Via one or a combination of these mechanisms, biomasses sequester pollutants from aqueous solutions. Although raw biomasses are effective in pollutant uptake, surface modification, as well as functionalization, increases the sorption capacity. Thermal and acid treatment increase sorbent porosity and subsequently its sorption capacity [4, 5]. Commonly used activating agents are KOH, NaOH, H3PO4, H2SO4, ZnCl2, among others [19]. Highly porous-activated carbons have been prepared from various crop

![Figure 2. (a) Fibrous surface of I. gabonensis bioadsorbents (Source: Authors); (b) moderately large pores on the surface of R. hookerie bioadsorbent (Source: Authors).](http://dx.doi.org/10.5772/66102)
residues using different activating agents. Prepared porous-activated carbons have been applied to the uptake of dyes and heavy metals and a few of previously reported work is summarized in Table 1.

<table>
<thead>
<tr>
<th>Crop residue</th>
<th>Treatment</th>
<th>Surface area (m²/g)</th>
<th>Pollutants</th>
<th>qₘₐₓ (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn cob</td>
<td>Thermal/H₃PO₄</td>
<td>600–700</td>
<td>Methylene blue</td>
<td>0.81–28.65</td>
<td>[20]</td>
</tr>
<tr>
<td>Palm stem</td>
<td>Thermal/K₂SO₄</td>
<td>–</td>
<td>Methylene blue</td>
<td>149</td>
<td>[21]</td>
</tr>
<tr>
<td>Rambutan peel</td>
<td>Microwave induced KOH activation</td>
<td>971</td>
<td>Acid yellow</td>
<td>215.05</td>
<td>[22]</td>
</tr>
<tr>
<td>Olive mill</td>
<td>Thermal/KOH</td>
<td>1641</td>
<td>Cr (III)</td>
<td></td>
<td>[23]</td>
</tr>
<tr>
<td>Pineapple waste</td>
<td>ZnCl₂/Thermal</td>
<td>914.67</td>
<td>Methylene blue</td>
<td>288.34</td>
<td>[24]</td>
</tr>
<tr>
<td>Grape waste</td>
<td>ZnCl₂/Thermal</td>
<td>1455</td>
<td>Methylene blue</td>
<td>417</td>
<td>[25]</td>
</tr>
<tr>
<td>Silkworm cocoon</td>
<td>(NH₄)₂HPO₄/KOH Activation</td>
<td>1153–2797</td>
<td>Congo red</td>
<td>512 g/kg</td>
<td>[26]</td>
</tr>
<tr>
<td>Durian seed</td>
<td>Thermal/KOH</td>
<td>980.62</td>
<td>Methyl red</td>
<td>384.62</td>
<td>[27]</td>
</tr>
<tr>
<td>Tomatoe waste</td>
<td>ZnCl₂/Thermal</td>
<td>1093</td>
<td>Methylene blue</td>
<td>400</td>
<td>[28]</td>
</tr>
<tr>
<td>Peanut shells</td>
<td>Microwave irradiation Pyrolysis</td>
<td>370.10</td>
<td>Direct black</td>
<td>110.6</td>
<td>[29]</td>
</tr>
<tr>
<td>Potato peels</td>
<td>H₃PO₄/Thermal</td>
<td>1.04</td>
<td>Co²⁺</td>
<td>373–480</td>
<td>[30]</td>
</tr>
<tr>
<td>Guava seed</td>
<td>Carbonization and physical activation</td>
<td>1000</td>
<td>Pb²⁺</td>
<td>96</td>
<td>[31]</td>
</tr>
<tr>
<td>Tropical almond</td>
<td></td>
<td>112</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Activated carbon preparation from different crop residue and their applications in dyes and heavy metal uptake.

1.1.2. Pretreatment methods and biosorbent efficiency

Surface treatment, modification, and/or functionalization enhance biosorption efficiency of bioadsorbents. The desired feature can be created in bioadsorbents via designed treatment and/or modification. Biomass treatment using concentrated acid may blow up the fibers subsequently leading to mesopore creation on biomass surface [5]. Mesopores are large enough to transport dyes into the bioadsorbents. The release of adventitious water from the biomass framework via thermal treatment may also result in generation of pores [4]. Texture and porosity of biomass can also be altered by microwave irradiation. Hollows, pores, and cavities serve as transport medium for the adsorbate into bioadsorbents [32].

The possibility of surface modification and/or functionalization gives additional advantage to crop residue. The surface of raw bioadsorbents may be tailored toward specific pollutants
via the introduction of specific functional group(s) that has(ve) affinity for the desired pollutant.

Surface modification may involve the grafting of functional group(s) onto the biomass frameworks, which have a high tendency to reduce sorbent porosity and subsequently its surface area [33, 34]. Interestingly, surface modified biomaterial usually generates adsorbents with far superior adsorption capacity. Sections 1.21 and 1.22 of this chapter introduced the possibility of pollutants uptake onto biomass via surface functional groups. Introduction of such functional groups with unique metal/dye binding characteristics enhances biomass sorption capacity. Metal ions can be complexed by thiol, amino, carboxylates, nitrogen, and oxygen-based moieties. Bonding via electrostatic interactions can also occur between metal and unprotonated carboxyl, oxygen, and sulphate groups. Table 2 compares some reported literature works that reveal increase in sorption potential of modified biomass over their unmodified counterparts.

<table>
<thead>
<tr>
<th>Crop residue</th>
<th>Pollutants</th>
<th>$q_{max}$ (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Citrus sinensis</em></td>
<td>Reactive yellow</td>
<td>36.36</td>
<td>[35]</td>
</tr>
<tr>
<td>Raw</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Immobilized</td>
<td></td>
<td>51.47</td>
<td></td>
</tr>
<tr>
<td>Chemically treated</td>
<td></td>
<td>106.36</td>
<td></td>
</tr>
<tr>
<td><em>Citrus sinensis</em></td>
<td>Reactive red</td>
<td>18.28</td>
<td>[35]</td>
</tr>
<tr>
<td>Raw</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Immobilized</td>
<td></td>
<td>39.06</td>
<td></td>
</tr>
<tr>
<td>Chemically treated</td>
<td></td>
<td>31.45</td>
<td></td>
</tr>
<tr>
<td><em>Irvingia gabonensis</em></td>
<td>Rhodamine B</td>
<td>212.77</td>
<td>[5]</td>
</tr>
<tr>
<td>Raw</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid treated</td>
<td></td>
<td>232.00</td>
<td></td>
</tr>
<tr>
<td><em>Lagerstroemia speciosa</em> bark</td>
<td>Cr (VI)</td>
<td>20.41</td>
<td>[36]</td>
</tr>
<tr>
<td>Raw</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HNO$_3$ modified</td>
<td></td>
<td>24.39</td>
<td></td>
</tr>
<tr>
<td><em>Phytolacca americana</em> L</td>
<td>Pb(II)</td>
<td>13.19</td>
<td>[37]</td>
</tr>
<tr>
<td>Raw</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HNO$_3$ modified</td>
<td></td>
<td>14.51</td>
<td></td>
</tr>
<tr>
<td>Charred dika nut waste</td>
<td>Rhodamine B</td>
<td>52.90</td>
<td>[4]</td>
</tr>
<tr>
<td>Raw</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chitosan coated</td>
<td></td>
<td>217.39</td>
<td></td>
</tr>
<tr>
<td><em>Eucalyptus sheathiana</em> bark</td>
<td>Zn (II)</td>
<td>128.21</td>
<td>[38]</td>
</tr>
<tr>
<td>Raw</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH modified</td>
<td></td>
<td>250.00</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Comparing the efficiency of raw and modified biomass.
1.1.3. Crop residue in dyes and heavy metal biosorption

Crop residues, based on their versatility earlier described, have been widely used in the uptake of diverse range of pollutants. Pollutants of interest here are dyes and heavy metals. This section, therefore, presents some recent works reported in literatures using crop residues in dye and heavy metal sorption.

The uptake of Cu (II) ions using almond shell has been reported. Binary metal mixture viz Cu (II) and Pb (II) was used in this study. The presence of lead was reported to affect copper uptake due to competition for sorption sites. The affinity of Pb (II) for almond shell was reported to be higher than that of Cu (II). While equilibrium sorption fitted best into the Sips model, maximum sorption was obtained to be 9.0 and 13.7 mg/g for Cu (II) and Pb (II), respectively [39]. Water chestnut peel was used in the uptake of Rhodamine B dye from aqueous solution with consideration of various sorption operational parameters. Heterogeneous sorption controlled by both liquid film and intraparticle diffusions was reported for the sorption mechanism. Adsorption data fitted best into the Freundlich isotherm model [40]. The use of *Trichoderma reesei* in the uptake of Co2+, Cu2+, Ni2+, Pb2+, and Zn2+ ions has been reported with consideration of various sorption operational parameters. While the uptake of the metal ions onto the bioadsorbents obeyed the Pseudo second kinetics models, biosorption process was affirmed to be spontaneous and feasible [41].

The uptake of Pb (II) from aqueous solution onto peanut shells has been reported. Decrease in bioadsorbents efficiency was observed with increased temperature. Equilibrium sorption data fitted best into the Langmuir isotherm model with maximum monolayer sorption capacity of 39 mg/g [42]. Batch sorption of Cd2+ onto *Arundo donax* reed leaves has been reported. Cd2+ removal was reported to be pH-dependent, and fast sorption kinetics was observed. The maximum monolayer sorption capacity was reported to be 27.90 mg/g. Equilibrium sorption data was best described by the Freundlich isotherm model, while the kinetic data best obeyed the pseudo second-order kinetics model [43]. The uptake of Cr (VI) using cork powder has been investigated and reported. Sorption parameters, such as contact time, pH, and concentration of Cr (VI), showed significant effects on pollutant uptake, and maximum uptake was observed between pH 2 and 3 [44]. The use of loquat (*Eriobotrya japonica*) leaves waste in Cd (II) uptake was investigated and reported. Uptake of Cd (II) was reported to be dependent on solution pH, initial cadmium ion concentrations, biosorbent dose, contact time, and temperature. Uptake of Cd (II) onto loquat leaves occurred via endothermic process; thus, bioadsorption was more favored at a high temperature. Equilibrium sorption data fitted well into both the Langmuir and Temkin isotherm models [45]. Removal of Malachite green using pea shells (*Pisum sativum L*) has also been studied and reported. Optimum operational parameter was established, and equilibrium sorption data was tested with some isotherm models. Freundlich isotherm model best described the sorption process, and pseudo second-order kinetics best explains the kinetics data [46]. Chir pine sawdust in the bioadsorption of Congo red and basic violet from aqueous has been reported. Equilibrium was attained between 45 and 60 min. While the equilibrium sorption data for the uptake of basic violet obeyed the Langmuir isotherm model, Freundlich isotherm model best described the uptake of Congo red onto the bioadsorbents. Maximum monolayer sorption capacity was 11.3 and 5.8 gkg for basic
violet and Congo red, respectively. Chemisorption was reported for the uptake of Congo red onto Chir pine sawdust, while physical sorption ruled the uptake of basic violet onto Chir pine sawdust [47].

The use of water hyacinth leaves in the uptake of amaranth (acid red 27) anionic dye has also been reported. The effects of various operational parameters were reported, and the dye uptake depended greatly on these effects. Dye uptake was reported to increase with increased contact time and dye concentration. Sorption kinetic data was best explained by pseudo second-order kinetic model, while the equilibrium sorption data fitted best into the Langmuir isotherm model with 70 mg/g [48]. Nauclea diderrichii seed biomass with low surface area was used for the uptake of toxic Cr (III), and it was found to be effective. Fast kinetics was reported for this study, with data fitting best into the pseudo second-order kinetics. Equilibrium sorption data was reported to fit best into the Freundlich isotherm model, and the maximum monolayer sorption capacity was 483.81 mg/g [49].

The effectiveness of oat hull in the removal of malachite green was investigated and reported. Optimum sorption condition was established, and the pseudo second-order kinetic models best described sorption kinetic data. High temperature favored the uptake of malachite green, while the Freundlich isotherm model best described the sorption equilibrium data. The maximum monolayer sorption capacity was reported to be 83 mg/g [50]. The use of R. hookerie fruit epicarp in the removal of Rhodamine has been investigated and reported. The prepared bioadsorbents were found to be effective in the removal of the pollutants. Freundlich isotherm best described the equilibrium sorption data, and maximum monolayer sorption capacity was reported to be 666.67 mg/g [2].

1.1.4. Conventional methods versus biosorption

The preference for adsorption over other wastewater treatment techniques relates to its simplicity of operations and ability to remove pollutants of very low concentration. Biosorption, however, adopts the aforementioned characteristics as well as abundance, availability, and economic advantages. In order to attain zero pollution outflows by most industries, combinations of methods are employed. While adsorption may act effectively in the removal of residue concentration as well as protects resins, ion exchange resins are very efficient in the combat of highly metal-loaded wastewater [51]. The application of activated carbon, ion exchange resins, chelating resin, and bioadsorbents by batch adsorption in removal of metal ions from real and aqueous effluents is summarized in Table 3.

In conclusion, the uptake of dyes and heavy metals onto various crop residues has been widely investigated. Amazing results of their efficiency were recorded. Freundlich isotherms that suggest a multilayer sorption commonly describe the sorption process. With the understanding that sorption onto crop residue may either be via functional group or available pores or the combination of the two, multilayer sorption may be expected often in pollutant uptake using plant residue.

Optimum operational parameters that can give insight into further applications were well studied and reported. However, only a few reports exist for applications of biomass to real
industrial effluent. Result-oriented applications of crop residues to real industrial effluents present a solution to the lingering challenge of water pollution. Real industrial effluents are a composite of various ions and other materials such as starch and salt. Thus, pilot studies using binary/ternary effluents as well as dye-metal mixture will assist in understanding the behavior of crop residue in real industrial effluent applications.

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Pollutants</th>
<th>Percentage (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion exchange resin (mix)</td>
<td>Cr</td>
<td>68.18~about 85%</td>
<td>[52]</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>82.09~87.25%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>58.33~about 90%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>50.00~75.58%</td>
<td></td>
</tr>
<tr>
<td>Chelatin resin</td>
<td>Cr</td>
<td>6.67~69.23%</td>
<td>[52]</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>54.48~85.19%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>25.00~87.50%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>11.11~39.54%</td>
<td></td>
</tr>
<tr>
<td>Activated carbon</td>
<td>Cr</td>
<td>46.67~about 85%</td>
<td>[52]</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>40.74~82.35%</td>
<td></td>
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<tr>
<td></td>
<td>Fe</td>
<td>58.33~83.33%</td>
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</tr>
<tr>
<td></td>
<td>Ni</td>
<td>5.26~11.11%</td>
<td></td>
</tr>
<tr>
<td>Ion exchange resin (INDION225H)</td>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>9.01~14.49%</td>
<td>[51]</td>
</tr>
<tr>
<td></td>
<td>50~100 mg/L</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eucalyptus bark</td>
<td>Zn&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>33.75~40.12%</td>
<td>[38]</td>
</tr>
<tr>
<td></td>
<td>20~70 mg/L</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Olive stone</td>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>6.61~19.87%</td>
<td>[53]</td>
</tr>
<tr>
<td></td>
<td>10~300 mg/L</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pine bark</td>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>35.25~76.00%</td>
<td>[53]</td>
</tr>
<tr>
<td></td>
<td>10~300 mg/L</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peanut shell</td>
<td>Pb&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>65.73%</td>
<td>[42]</td>
</tr>
<tr>
<td></td>
<td>100 mg/L</td>
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</tbody>
</table>

Table 3. Comparison of pollutant removal techniques and percentage removal.

...
1.2. Biomass valorization in phytomedicine

The use of plant materials as sources of beneficial nutritional component dates back to prehistoric time. Noah obtained alcohol from vine as recorded in the Bible; Hippocrates encouraged the consumption of medicinal food [54], and the list continues.

Centuries later, several plants have been identified as sources of phytochemicals with potent medicinal value. Initially, plant extracts were used directly, but in these modern times, bioactive extracts are fractionated, and pure compounds isolated therefrom are then investigated for their inherent pharmacological properties. This, of course, is preceded by the characterization of the isolates using spectroscopic tools such as 1D and 2D-Nuclear Magnetic Resonance, Infrared, and mass spectrometry.

Despite the advent of several synthetic drugs via improved scientific methods of drug development, natural products have continued to maintain relevance by consistently providing new compounds with interesting structural motifs, which serve as sources of new drug leads.

The consequence of this intense plant utilization is the generation of a huge amount of waste, which eventually constitutes environmental pollution among other problems. In line with waste valorization, which promotes environmental sustainability, several scientists have engaged in intense search into possible economically beneficial application of plant wastes.

In the same vein, the discovery of beneficial phytochemicals in waste plant materials would be a welcome development for scientists. This is because there would not be any threat to food security as is the case when an edible food source is found to supply uniquely valuable phytochemicals [55].

This section is, therefore, dedicated to the interesting medicinal application of phytochemicals obtained from waste biomasses.

1.2.1. Direct application of plant parts

Conventionally, the active components in different plant parts are first extracted with the aid of a suitable solvent, for example, water and ethanol. The extract solution is then concentrated to obtain the crude extract, which is then applied to proffer solution to different health challenges.

However, these same plant parts can be used directly for different purposes without conventional extraction. An example of such usage is the use of banana leaves, plantain leaves, and *Thaumatococcus daniellii* in food packaging. Particularly, these leaves have been employed in the packaging of bean pudding. Although the initial reason for employing these leaves as packaging materials was their surface area and their ability to withstand heat, it has also been observed that these leaves perform additional functions such as flavour enhancement and possible supply of medicinal compounds to the consumer [56]. Quantitative phytochemical analysis of the leaves of *T. daniellii* prior to and after usage revealed that some of these phytochemicals (saponins, flavonoids, and tannins) have leached either into the bean pudding or the water used for steaming [57].
It will be interesting to initiate a research that will reveal the exact position of these leached phytochemicals as the presence of saponins in food samples could constitute a natural preservative, which will prevent the growth of food spoilage organisms such as *Escherichia coli*. Saponins have been earlier implicated in antimicrobial activity [58]. Similarly, the presence of flavonoids in bean pudding would be advantageous since they are potent scavengers of free radicals in human systems.

Furthermore, agro-wastes can be utilized in biotreatment procedure for safe long-term storage of cereal products. An example is the inhibition of *Aspergillus parasiticus* and aflatoxin production during the storage of wheat, rice, and maize by powdered neem (*Azadirachta indica*) and kika leaves (*Acia nilotica*). The agro-wastes (leaves) in their powdered forms were applied to the cereals at three concentrations 5, 10, and 20% out of which 20% neem gave the best overall result. Neem leave powder is, therefore, a safe and cheap natural additive for the improvement of the storage of selected cereal products [59]. Similarly, pomegranate peels powder at 1–3% concentration have been shown to provide high storage stability in prepared beef sausage samples, and the presence of antimicrobial/antioxidant phenolics explains this important activity [60].

1.2.2. Extraction of phytochemicals from waste biomass

In several homes, various plant parts such as lemon grass and tea have been boiled in water in order to obtain tonics, which are drunk afterward to achieve different objectives. This domestic procedure is known as extraction.

Extraction, in this context, is the process of separating active constituents or secondary metabolites of interest from waste plant matrix by the use of extractants (solvents). Different methods of extraction that have been utilized in the extraction of phytochemicals include the following:

1.2.2.1. Maceration and percolation

These are cold traditional methods of extraction in which water or organic solvents are made to permeate pulverized biomass with the aim of transferring the phytochemicals in the biomass into the solvent. The extract solution is afterward concentrated using an appropriate technique, for example, rotary evaporator to obtain the crude extract. While maceration emphasizes soaking the biomass in the choice solvent to achieve the extraction, percolation involves the permeation of the solvent through the biomass in the direction of gravity and filtration in order to obtain the extract solution. These traditional methods of extraction have been employed in the extraction of phytochemicals from sweet potato peels, leading to extracts and isolates with antioxidant and antifungal properties [1].

Although these methods may not be as fast as other methods discussed in this section, they do preserve phytochemicals which are thermolabile by nature, thus retaining the pharmacological activities of interest.

1.2.2.2. Hydrodistillation/assisted hydrodistillation

Hydrodistillation (HD) is a method, which is employed for the extraction of fragrances/flavors from plants. In principle, the vapors of the volatile constituents are conveyed by steam to a
condenser, where they are returned to liquid state and form two layers: aqueous and oil-rich layers. The two methods via which hydrodistillation is executed are steam distillation and Clevenger distillation [61]. This important extraction method yielded the essential oils from tangerine peels, which were successfully adopted for fish preservation [62].

In recent times, the conventional HD has been assisted and improved with ohmic and micro-wave heating processes. Assisting hydrodistillation with ohmic heating reduced the extraction time by over 50%, that is, from 1 h to 24.75 min [63], while the GC-MS analysis conducted did not show any difference in the chemical constitution of the oil. Although a shorter extraction time was achieved using the microwave-assisted hydrodistillation [64], the ohmic-assisted HD was the greener method of extraction since its energy consumption is relatively low.

1.2.2.3. Soxhlet extraction

This is a hot method of extraction in which the soxhlet apparatus is employed to achieve the extraction process. The soxhlet apparatus is depicted in Figure 3.

This method was successfully utilized in our laboratory to extract constituents of Ipomoea batatas peel-waste [65]. Although this method has good speed and high yield as advantages, the possibility of thermal decomposition of the active principles remains a subject of huge concern and constitutes a limitation to this application.

1.2.2.4. Pressurized fluid extraction

One of the emerging methods that have been employed for extractions from waste biomass is pressurized fluid extraction (PFE). We will focus on two PFE methods in this section: supercritical extraction and subcritical extraction.

Supercritical extraction is an extraction method in which the conventional solvent has been replaced by a supercritical fluid: a supercritical fluid is a liquid substance at a temperature and

Figure 3. Three soxhlet apparatus on heating mantles during the hot extraction of the phytochemicals in water melon rind (Source: Authors).
pressure above its critical point—a point where distinct liquid and gas phases do not exist. A common example of this supercritical fluid is CO₂, which is sometimes modified by cosolvents such as ethanol and methanol [66]. This environment friendly method was successfully applied to citrus peels, a common by-product in citrus processing industries [66]. Fatty acid esters, phenols, coumarin derivatives, and terpene derivatives were among the useful compounds that were isolated in the process.

Although more expensive to set up, the advantage of this method is its environmental friendliness and extremely easy solvent removal.

The cost cut by improved percentage yield achieved by PFEs has not been compared with the cost of setting up pressurized fluid extraction apparatus. Despite this gap, the safety guaranteed by the absence of obnoxious chemicals continues to make PFE a preferred alternative.

In the same vein, subcritical water (pressurized hot water) has also been employed to achieve environment friendly extractions. Subcritical water is water under 0.2–21 MPa pressures and temperatures higher than its boiling point but lower than its critical temperature. Subcritical water was first reported in 1994 [67], and several other applications of subcritical water has been reported since then. Recently, this method was applied to several agro-waste biomasses in Canada. These waste biomasses are potato peel, barley hull, lentil husk, and flaxseed hull as contained in a recent review by Saldana and Valdivieso-Ramírez [68].

1.2.3. Effect of extraction method on bioactivity

The different extraction conditions associated with different extraction methods have considerable effect on the pharmacological potency of various phytochemicals. Such conditions include the following:

- Extraction pressure
- Extraction time
- Extraction solvent
- Extraction temperature

Trabelsi et al. studied the effect of high pressure (300 and 500 MPa) and time (3 and 10 min) on the antioxidant/antimicrobial activity of citrus peel extracts [66]. While the antimicrobial activity was not at all influenced by high pressure, the highest Total Phenolic Content (TPC) and antioxidant capacities were observed at 300 MPa and 3 min. Extraction at higher temperature and longer time probably drew out more “nonantioxidant” matter or decomposed some antioxidant constituents in the extracts, thus reducing the TPC per gram.

Furthermore, extraction solvent and extraction time have significant effect on the antimicrobial activity of bioactive extracts from watermelon seeds as shown by a recent study from the School of Science, Landmark University, Nigeria [58]. Cold methanol extract was more active against *Staphylococcus aureus* compared with the hot methanol extract. Thermal decomposition might have affected some of the phytochemicals that are responsible for the observed activity.
Furthermore, the cold chloroform extract that did not inhibit the growth of *S. aureus* at all was, however, active against *Pseudomonas aeruginosa*. This simply shows that the choice of a solvent in phytochemical extraction greatly influences the nature of compounds extracted and ultimately the biological activity of the extract. The effect of different extraction methods on percentage yield and bioactivity is vividly displayed in Table 4.

Generally, the introduction of pressure, higher temperature, and supercritical fluids led to the achievement of better yields and improved/preserved biological activity.

### 1.2.4. Medicinal products from waste biomass

Different kinds of plant biomass have been employed in the search for medicinal phytochemicals. Selected examples are shown in Table 5.

In line with the principles of green chemistry, waste biomass that otherwise would have been discarded have been exploited as sources of beneficial/medicinal phytochemicals by several research scientists.

#### 1.2.4.1. Antioxidants from waste biomass

Antioxidants, as the name implies, are compounds that oppose or prevent oxidation. They are compounds that scavenge free radicals, which have been known to cause unwanted oxidation of important molecules in the body.

\[ \text{R} + \text{ArOH} \rightarrow \text{RH} + \text{ArO} \]  

The unwanted free radical (R) is reduced by the antioxidant compound (ArOH), resulting in the harmless RH and ArO which is a more stable radical.

Furthermore, a high consumption of antioxidants has been correlated with lower incidence of cancer [82]. During renovation of cultivations, the roots of *Rugosa rose* are usually treated as wastes. Olech et al. studied, among other parameters, the antioxidant potential of this postharvest residue with the aim of proposing new uses for it. Interestingly, these roots displayed significant antiradical activity compared with ascorbic acid. Hence, these roots could be explored as a source of antioxidant supplements in food and pharmaceutical industries [83].

In the same vein, tomato-processing by-products (TPP) have also been shown to contain antioxidants. Particularly, the presence of simple polyphenols in TPP suggests that it could be safely used as a functional ingredient in the production of antioxidant-rich foods [84].

Similarly, Oluyori et al. recently reported a successive extraction of sweet potato peels using ethyl acetate and methanol, respectively. While the extracts did not show significant antimicrobial activity against the selected microorganisms, the DPPH assay and the TPC determination revealed the methanolic extract as the extract with higher antioxidant capacity [6].

These and many other research efforts continue to prove that there is, indeed, a vast amount of wealth in agro wastes, which are usually discarded.
<table>
<thead>
<tr>
<th>S/No</th>
<th>Extraction method</th>
<th>Process condition</th>
<th>Percentage of yield (%)</th>
<th>Remarks</th>
<th>Reference (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Room temperature hot water extraction</td>
<td>25 °C; 3 h; 1:20; w/v</td>
<td>&lt;30.35%</td>
<td>% yield of CPS by microwave-assisted extraction was the highest and the antitumor activity same extract was the best</td>
<td>[69]</td>
</tr>
<tr>
<td></td>
<td>Hot water extraction</td>
<td>78 °C; 3 h; 1:20; w/v</td>
<td>&lt;30.35%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Microwave-assisted extraction</td>
<td>5 min; 280 W; 70°C; 1:20; w/v</td>
<td>30.35%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ultrasound-assisted extraction</td>
<td>13 min; 250 W; 45°C</td>
<td>&lt;30.35%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cellulase-assisted extraction</td>
<td>55°C; 80 min; pH 5.0</td>
<td>32.50%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ultra-high pressure extraction (UPE)</td>
<td>60% ethanol; 400 MPa; 2 min; 30°C; 1:5 solid to liquid ratio</td>
<td>4.395% chlorogenic acid</td>
<td>UPE showed higher extraction yield, shorter extraction time, lower energy consumption, and higher purity of extracts</td>
<td>[70]</td>
</tr>
<tr>
<td></td>
<td>Heat reflux extraction</td>
<td>60°C; 3 h</td>
<td>3.471% chlorogenic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ultrasonic extraction</td>
<td>250 W; 30°C; 40 min; 42 KHz</td>
<td>3.601% chlorogenic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Soxhlet extraction</td>
<td>60°C; 2 h</td>
<td>3.793% chlorogenic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ultra-high hydrostatic pressure (UHP)</td>
<td>60% ethanol; 70:1 ml/g solvent: herb; 500 Mpa hydrostatic pressure; 3 min</td>
<td>26.12%</td>
<td>High efficiency at room temperature was observed for UHP; flavanoids and salidroside were used to monitor the extraction yield</td>
<td>[71]</td>
</tr>
<tr>
<td></td>
<td>Reflux extraction</td>
<td>80°C; 120 min; 4:1 ml/g</td>
<td>13.83%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Soxhlet extraction</td>
<td>80°C; 240 min;</td>
<td>17.00%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Supercritical fluid extraction (SFE)</td>
<td>250 bar and 40°C</td>
<td></td>
<td>SFE gave the best extraction yield and the most active extract</td>
<td>[72]</td>
</tr>
<tr>
<td></td>
<td>Soxhlet extraction</td>
<td>Ethanol; 6 h</td>
<td>10.00%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Steam distillation</td>
<td>4 h</td>
<td>0.60%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Marceration</td>
<td>40°C; 48 h; material: solvent 1:10</td>
<td>8.90%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1.2.4.2. Antimicrobial compounds from waste biomass

The emergence of multidrug-resistant bacteria has continued to be a major concern across the globe. This is the reason for the increased attention given to the search for new antimicrobial agents.

Generally, many people after consumption discard the seeds of watermelon. However, several scientists have now shown that inherent in these seeds are phytochemicals with varying activities against *Staphylococcus* sp., *E. coli*, *Proteus* sp., *Klebsiella* sp., and *P. aeruginosa* [57]. Hence, these seeds could serve as renewable sources of new antimicrobial agents.

A similar study focused on the valorization of sweet potato peels. It was interesting to have isolated beneficial triterpenoids from sweet potato peels that we normally discard. Although the isolates (an example is shown in Figure 4) from the peels of *I. batatas* Lam exhibited low

---

<table>
<thead>
<tr>
<th>S/No</th>
<th>Extraction method</th>
<th>Process condition</th>
<th>Percentage of yield (%)</th>
<th>Remarks</th>
<th>Reference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Soxhlet extraction</td>
<td>720 min; 200 ml solvent</td>
<td>9.58%</td>
<td>% yield of scopoletin was used to determine the extraction efficiency</td>
<td>[73]</td>
</tr>
<tr>
<td></td>
<td>Reflux extraction</td>
<td>480 min; 100 ml solvent</td>
<td>10.95%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ultrasound-assisted extraction</td>
<td>20 min; 60 W; 50 ml solvent</td>
<td>28.55%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Microwave-assisted extraction</td>
<td>1 min; 560 W; 50 month = 1 solvent</td>
<td>45.10%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Supercritical fluid extraction</td>
<td>60 min; 6500 psig;</td>
<td>7.99%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Steam distillation</td>
<td>403–423 K; 24 h; atm pressure</td>
<td>2.32%</td>
<td>% yield of essential oil from Kabosu (<em>Citrus sphaerocarpa</em>) peel was used to measure the extraction efficiency</td>
<td>[74]</td>
</tr>
<tr>
<td></td>
<td>Supercritical fluid extraction</td>
<td>313–352 K; 10–30 Mpa; 0.19–0.21 g/s CO2 flow rate</td>
<td>1.55%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cold press</td>
<td>100 ml distilled water; centrifuged at 10,000 G for 15 min/frozen at 253 K</td>
<td>0.12%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Supercritical fluid extraction</td>
<td>600 bar/40°C</td>
<td>88.20 mg/100 g oil</td>
<td>Extraction of tocopherols</td>
<td>[75]</td>
</tr>
<tr>
<td></td>
<td>n-hexane extraction</td>
<td>600 bar/80°C</td>
<td>85.57 mg/100 g oil</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>—</td>
<td>—</td>
<td>62.38 mg/100 g oil</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Different extraction methods: process conditions and effects on percentage(%) of yield.

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1.2.4.2. Antimicrobial compounds from waste biomass

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A similar study focused on the valorization of sweet potato peels. It was interesting to have isolated beneficial triterpenoids from sweet potato peels that we normally discard. Although the isolates (an example is shown in Figure 4) from the peels of *I. batatas* Lam exhibited low
antibacterial activity, the same isolates were more active against two fungi: *Tricophyton metagrophytes* and *Sporothrix schenkii* (IC50, 50 μg/ml) [1].

Similarly, extracts from drumstick peel recently exhibited significant activity against two human pathogenic bacteria: *S. aureus* and *E.coli*. This extract, which was nontoxic to red blood cells, also showed some photocatalytic property [85].

<table>
<thead>
<tr>
<th>S/No</th>
<th>Biomass type</th>
<th>Plant source</th>
<th>Medicinal phytochemical of interest</th>
<th>Application</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Seed</td>
<td>Sour cherry seed kernel</td>
<td>Alpha-tocopherol, tocotrienols, tocopherol-like compounds</td>
<td>Antioxidants</td>
<td>[76]</td>
</tr>
<tr>
<td>2</td>
<td>Stem bark</td>
<td><em>Mitrephora celebica</em></td>
<td>Ent-tradyloban-19-oic acid and ent-kaur-16-en-19-oic acid</td>
<td>Antimicrobial</td>
<td>[78]</td>
</tr>
<tr>
<td>3</td>
<td>Leaves</td>
<td><em>Leaves of X. laavigata</em></td>
<td>Essential oils (γ-umurolene, δ-cadinene, α-copaene, germacrene-D, bicyclogermacrene and (E)-cariophyllene</td>
<td>Antitumor activity</td>
<td>[79]</td>
</tr>
<tr>
<td>4</td>
<td>Leaves</td>
<td><em>Leaves of Clinacanthus nutans lindau</em></td>
<td>13(2)-hydroxy-(13(2)-R)-phaephytin b, 13(2)-hydroxy-(13(2)-R)-phaephytin a, 13(2)-hydroxy-(13(2)-S)-phaephytin a</td>
<td>Anti-herpes simplex activity, Anti-HSV-IF activity</td>
<td>[80]</td>
</tr>
<tr>
<td>5</td>
<td>Flowers</td>
<td>Elder flower: <em>Sambucus nigra</em></td>
<td>Naringenin</td>
<td>Nutraceutical application (modulation of glucose metabolism)</td>
<td>[81]</td>
</tr>
<tr>
<td>6</td>
<td>Peels</td>
<td>Sweet potato peels</td>
<td>3-Friedelanol; Stigmasterol; Urs-13(18)-ene-3β-yl acetate</td>
<td>Antifungal</td>
<td>[1]</td>
</tr>
</tbody>
</table>

*Table 5. Different plant biomass sources and the phytochemicals of interest.*

*Figure 4. A natural antifungal compound from sweet potato peel: Urs-13(18)ene-3β-yl acetate (Source: Authors).*
1.2.4.3. Anticancer compounds from waste biomass

Cancer is the second leading cause of death in the United States after heart disease. In fact, it has been said to be responsible for one out of every four deaths [86]. Although there are current cures for cancer, the high cost of treatment is a challenge to many cancer patients. In view of the increasing cost of cancer treatment, the presence of anticancer compounds in waste biomass is a blessing to many, especially, people in the developing world [87]. The roots of R. rose, which showed some antiradical activity as earlier mentioned, also exhibited significant anticancer potential. About 90% inhibition of cervical (HeLa) and breast (T47D) cancer cell lines was observed in the presence of the rugosa root extracts, showing that the roots that have hitherto been ignored are an important phytochemical source [83]. Similarly, Oluyori et al. recently carried out an anticancer guided fractionation/isolation of an alcoholic extract from sweet potato peels [88]. An anticancer fraction was obtained, and a glucocerebroside \( \text{N-((E)-3,4-dihydroxy-1-(((2R,3R,4S,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)octadec-8-en-2-yl)-2-hydroxytetracosanamide} \) was isolated and characterized as the main anticancer compound. Our results suggest that the consumption of sweet potato peels may supply the body with phytochemicals that can prevent the onset or the development of cancer [89]. These findings among others project agro-wastes as potential sources of economically important compounds with multifaceted medicinal applications.

1.3. Harnessing agro-wastes for bioethanol production

Conversion of agricultural waste into fuel has become popular in the past few decades occasioned by the increasing demand for fossil fuel. Campbell and Laherrere [89] had predicted the reduction in availability of “cheap fuel” years ago. In a bid to forestall imminent fall in supply, many countries ventured into research seeking alternative energy sources. This led to the production of biofuel from various sources including cornstarch, sugar cane, and now from cellulosic biomass. Biofuels have several advantages over fossil fuel including being environment friendly, thus reducing pollution. There is also a reduction in the release of greenhouse gases and consequent global warming [90]. Biofuels are produced from renewable sources such as rind of various fruits, corn stover, “weeds” including switch grass, winter rye, and faba bean to mention a few [91]. This section elaborates the extent of research on bioethanol production from agricultural wastes, exposes possible challenges in bioethanol production from agro-wastes as well as exposes gaps from various previous research works efforts thus opening new areas of investigations to researchers.

1.3.1. A drift to biofuel as an alternative energy source

Biofuels are any kind of fuel made from living things or from the wastes they produce [92]. Biofuels can also be referred to as renewable energy produced from organic matter by converting its complex carbohydrates into energy. The carbon dioxide (CO\(_2\)) emitted during biofuel production is not larger than that consumed during photosynthesis. In order words, the process is CO\(_2\) neutral and beneficial to the environment as opposed to combustion of fossil fuels that leads to increase in greenhouse gases, which causes ozone layer depletion. Biofuels include biogas, biodiesel, and bioethanol, but bioethanol has enjoyed vast investment and is
popular as a transport fuel. It is presently the most widely used in the transport industry, and it is receiving attention at the international and national fronts [93]. Countries at the forefront of bioethanol production include the United States of America (USA) and Brazil. Blending ethanol with gasoline is advantageous because it brings about reduction in consumption of fossil fuel, and in recent time, bioethanol has provided a means of powering engines without using fossil fuels. Currently, there are vehicles that can run solely on bioethanol as well as in blends with gasoline, for example, E5, E10, and E5 implies that 5 parts of bioethanol is blended with 95 parts of gasoline. When gasoline is blended with bioethanol, it has a higher octane number, which implies that the engine has increased thermal efficiency and works more efficiently.

1.3.2. Second-generation bioethanol

For the production of bioethanol, sugars are fermented using yeast and other microorganisms. Commercial quantities of bioethanol have been produced from corn, sugar cane, sweet sorghum, and cassava [94]. Bioethanol produced in this manner is referred to as first-generation ethanol. In a bid to find feedstock that will not compete with (human) food and (animal) feed and also meet up with global demand for bioethanol production, second-generation bioethanol production was introduced [93]. This process exploits the use of lignocellulosic biomass such as agricultural wastes as feedstock because they are renewable, available in abundance, and relatively cheap. Utilization of such agricultural waste involves pretreatment of such waste, then hydrolysis of the pretreated material, and finally, fermentation of monomeric sugars released to yield bioethanol.

Lignocellulosic materials currently in use include agricultural wastes/residues; forest residues such as fallen branches, leaves, twigs, and sawdust, municipal solid wastes including paper and cardboard products as well as industrial wastes and energy crops. Energy crops include herbaceous crops such as switch grass, fast-growing hybrids of poplar and leucaena trees [95]. Among all these sources of lignocellulose, agricultural wastes/residues are the most abundant and provide higher quantities of cellulose. Agricultural wastes are parts of the plant that are left after the main crop has been obtained. Examples are corn stover, sugar cane bagasse, spent sugar beets pulp, sweet sorghum straw, cotton seed hairs, oil palm frond, and banana stem. All these can be converted into bioethanol to provide energy to drive various engines. These materials are of great advantage because the crop is grown for dual purpose: first, as a source of food or feed and second, to provide lignocellulosic biomass, which will serve as feedstock for bioethanol production. This is of great advantage to the farmer who now obtains economic value from both the crop and its waste.

1.3.3. Pretreatment technologies

As stated earlier, agricultural wastes undergo pretreatment, and hydrolysis before the fermentation of sugars can be carried out. Pretreatment is a process of solubilization and separation of one or more components of a biomass. In this case, the lignocellulosic material breaks down thereby making cellulose more susceptible to enzymatic attack [95]. The cell wall of agricultural waste consists of cellulose, hemicelluloses, and lignin. Of these three, cellulose, which is the highest constituent, is responsible for the mechanical strength of the
cell wall. The glucose monomers of cellulose are connected by β-1,4 glycosidic bonds; hemicellulose is a branched heteropolymer of D-xylose, L-arabinose, D-mannose, D-glucose, D-galactose, and D-glucuronic acid, while lignin is composed of three major phenolic components, namely p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol and other extractable components.

Various types of pretreatment ranging from physical, chemical to biological pretreatment have been described [96, 97]. Pretreatment is aimed at removing lignin and hemicellulose, reducing the crystallinity of cellulose, and increasing porosity of the lignocellulosic materials. Physical pretreatment could be a combination of mechanical methods whereby the waste materials are comminuted by chipping, grinding, and milling, leading to reduced cellulose crystallinity. Pyrolysis is another form of physical pretreatment that involves treating the agricultural waste at temperatures above 300°C. Another form of physical pretreatment of agricultural waste steam is explosion that involves heating the biomass to a desired temperature for a specified period of time [98]. Chemical pretreatment involves treating lignocellulosic material with chemicals, for example, ozonolysis necessitates using ozone to degrade lignin and hemicellulose. Acid [99] and alkaline pretreatments are other forms of chemical pretreatment using concentrated acids such as H₂SO₄ and bases, respectively, to treat lignocellulosic materials. Apart from the aforementioned chemical pretreatment methods, lignin degradation could be catalyzed by a process known as oxidative delignification in the presence of hydrogen peroxide. Combinations of physical, chemical, and biological pretreatment methods can be used on lignocellulosic agricultural waste [100, 101]. Examples of such methods are steam explosion (a physical pretreatment method) and ammonia fiber explosion (AFEX that is a chemical pretreatment method); ultrasonic (physical) pretreatment of rice hull followed by biological pretreatment with *Pleurotus ostreatus* [102].

Biological pretreatment is highly advocated as it can prevent the formation of inhibitory by-products that can adversely affect subsequent stages of hydrolysis and fermentation. Biological pretreatment is also said to be cost-effective, environment friendly compared with chemical methods. Brown rot, white rot, and soft rot fungi are currently used for biological pretreatment [103, 104].

Advantages of biological pretreatment include mild conditions to undertake the process and low energy requirements, ecofriendly, less hazardous to health, more economical, and more effective compared with other chemical and physiochemical methods of pretreatment [105]. White rot fungi has been recognized as efficient for lignin degradation, and their activity is said to enhance the subsequent enzymatic hydrolysis. These organisms degrade the lignin seal and thus give access to cellulases attack on cellulose, but this process is often slow, spanning from 28 days to about 120 days [104]. Apart from longer pretreatment period, biological pretreatment also requires a large space and carefully controlled growth conditions; sometimes the organisms used act on lignin as well as hemicellulose and cellulose [93, 103]. Agricultural wastes are abundant feedstock for bioethanol production; however, there is need to focus more on pretreatment preferably biological pretreatment in order to exploit the benefit of this feedstock for biofuel production.
1.3.3.1. Hydrolysis

After pretreatment, hydrolysis of cellulose is carried out; this involves the conversion of cellulose (and hemicelluloses) to monomeric sugars using chemicals or enzymes [97]. Cellulases are often used for enzymatic hydrolysis of the pretreated agricultural waste [103]. Enzymatic hydrolysis leads to the release of fermentable sugars from the pretreated waste. This process of enzymatic hydrolysis is dependent on some factors including pH of the reaction, temperature, substrates, time, and enzyme activity.

1.3.3.2. Fermentation

When hydrolysis and fermentation are carried out separately, it is called Single Hydrolysis and Fermentation (SHF), but when enzymatic hydrolysis and fermentation are carried out concurrently, the process is termed Simultaneous Saccharification and Fermentation (SSF). In another process known as simultaneous saccharification and cofermentation (SSCF), enzymatic hydrolysis of both glucose and hemicellulose is carried out followed by fermentation of the sugars (glucose and xylose) produced in the same vessel [104].

Consolidated bioprocessing, on the other hand, integrates cellulase production with hydrolysis and fermentation of lignocellulosic material for biofuel production. It has the advantage of potentially reduced production cost, higher energy input, and higher conversion efficiency. A major challenge has, however, been finding a suitable consortium of organism to drive this process. Organisms such as *Saccharomyces cerevisiae*, *Clostridium thermocellum*, and *C. phytofermentans* are, however, being genetically engineered to perform this purpose [3]. Agricultural residues such as winter rye straw, oilseed rape straw, and faba bean straw have been shown to yield 66, 70, and 52% (of theoretical calculation) ethanol after pretreatment by wet oxidation and fermentation by *S. cerevisiae* [106].

One of the challenges faced in the fermentation of monomeric sugars to ethanol is that ethanol produced in the medium is inhibitory to some organisms used for fermentation. In addition, certain products such as furfural and hydroxymethylfurfural will limit or totally stop the activities of organisms used for fermentation. Apart from these, other factors such as high temperature, osmotic stress, and contamination by other organisms can adversely affect the process. Eventually, the ethanol produced by fermentation is made to undergo distillation [97].

Bioethanol yield of 11.11% was obtained when preheated rice husk was treated with *Trichophyton soudanense* that was fermented with palm wine yeast. But without fungal treatment, the heat-treated rice husk did not give up to 5% bioethanol yield [107]. Also, the highest cellulose and lignin yields recorded from rice husk in their study were 44.50 and 28.90% obtained from rice husk pretreated with *Trichophyton mentagrophyte* and a coculture of *T. soudanense* and *T. mentagrophyte*, respectively, while the highest hemicellulose value of 30.50% was obtained from preheated rice husk treated with *T. soudanense*.

Agro-waste such as coffee mucilage has also been reported to produce bioethanol. Unlike some agro-wastes that require pretreatment, it was established that coffee mucilage could provide up to 60 g/L of reducing sugar, which could be directly converted to bioethanol using *S. cerevisiae* Y2034 [108]. Pretreatment of wild cassava peels (*Manihot glaziovii*) with enzymes
and a combination of enzyme with alkali followed by simultaneous saccharification and fermentation (SSF) was reported. Results revealed that the latter treatment led to higher ethanol production of about 95% theoretical yield [109].

Banana waste composed of approximately 14% of lignin, 14.8% of hemicellulose, and 13.2% of cellulose was reported to yield 7.45% v/v ethanol [95, 104]. Paulova et al. [110] also reported increased ethanol production as conversion of cellulose to glucose increased; in the same vein, as the quantities of furfural and hydroxymethyl-furfural reduced, ethanol yield increased. For example, 78% conversion of cellulose to glucose brought about 0.34 g/g yield of ethanol in the presence of 88 mg/l furfural and 6 mg/l hydromethyl-furfural. On the other hand, 64% cellulose to glucose conversion brought resulted in an ethanol yield of 0.04%, while 158 mg/g and 10 mg/g of furfural and hydromethyl-furfural were detected.

In conclusion, utilizing agricultural waste as energy source in the form of bioethanol is a viable way of converting waste to wealth. These wastes are available in abundance and renewable hence continuity in production of bioethanol is assured. Nevertheless, there is a need for further research on how to minimize production cost especially at the pretreatment stage. In the same vein, future research should focus on how to scale-up second-generation bioethanol production so that commercial production of bioethanol will not depend on food crops only.

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**References**


[66] Trabelsi, D., Aydi, A., Zibetti, G.W., Porta, D., Sconagmiglio, M., Cricchio, V., Langa, E., Abderrabba, M. and Mainar, A.M., Supercritical extraction from Citrus *Aurantium amara* peels using CO$_2$ with ethanol as co-solvent; The Journal of Supercritical Fluids; http://dx.doi.org/doi:10.1016/j.supflu.2016.07.003.


[86] Cancer facts and figures 2015, American Cancer Society.


