AGRICULTURAL WASTE AS A PANACEA FOR HIGH COST OF ELECTROCHEMICAL DOUBLE LAYER SUPER-CAPACITOR AND SUSTAINABLE ENERGY STORAGE SOLUTION: A REVIEW

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Abstract

Supercapacitors, also known as ultracapacitors or electrochemical capacitors, are energy storage devices that store and release energy quickly. They are used in various applications, including renewable energy systems, electric vehicles, and electronics. Using agricultural waste as a source for supercapacitor’s electrode materials is an innovative and sustainable approach that holds promise for addressing the high cost of these materials. Agricultural wastes, such as crop residues, husks, shells, and other byproducts, often presents challenges in terms of disposal and environmental impact but have proven to be a good precursor material for the synthesis of electrochemical super capacitor’s electrode. By repurpose these waste materials for supercapacitor electrodes, the high cost of the electrode will be reduced and hence the overall cost of the supercapacitors.

Keywords: Agricultural Waste, Costs, Super-capacitor, Sustainable, Energy and Storage

1.0 Introduction

Waste refers to any material or substance that is no longer useful or needed and is disposed of by throwing away, burning, or recycling [1-3]. This can include anything from household garbage, industrial waste, sewage, electronic waste, agricultural waste and hazardous waste. It is important to properly manage and disposed of waste to prevent pollution and protect the environment and public health[4, 5]. Agricultural waste refers to the various byproducts, residues, and materials generated as a result of agricultural activities[6, 7]. These wastes can come from both crop production and animal husbandry, and they have the potential to cause environmental problems if not managed properly[8, 9]. The amount of agricultural waste generated depends on various factors such as the type of crop grown, farming practice, and level of processing. Large-scale agricultural operations such as commercial farms and food processing plants tend to generate more waste than smaller operations[9, 10]. Agricultural waste can be a valuable resource when properly managed and recycled. For example, crop residues and animal manure can be used for composting and as a source of energy for biogas production. Recycling and managing agricultural waste can reduce greenhouse gas emissions, improve soil health and fertility, and reduce pollution in land, air and water. Agricultural waste can be categorized into different types based on their origin and characteristics[11, 12]:

i. Crop Residues: These are the leftover materials from harvested crops, such as stalks, leaves, husks, and stems. Crop residues are often used for purposes like animal feed, mulching,
or as a source of organic matter for composting.

ii. **Animal Manure:** Waste produced by livestock, poultry, and other animals on farms. Manure contains nutrients like nitrogen, phosphorus, and organic matter that can be beneficial for soil fertility when used appropriately. However, improper handling and disposal of manure can lead to water and air pollution.

iii. **Food Processing Waste:** Waste generated during the processing of agricultural products, such as peels, shells, and seeds. This type of waste can often be repurposed for animal feed, bioenergy production, or composting.

iv. **Packaging and Plastics:** Agricultural activities involve packaging materials for transporting and storing produce. These materials can contribute to plastic waste if not properly managed or recycled.

v. **Agrochemical Containers:** Pesticide and fertilizer containers can become waste after their contents are used. Proper disposal or recycling of these containers is crucial to avoid environmental contamination.

vi. **Spoiled or Unmarketable Produce:** Fruits, vegetables, or other produce that doesn't meet market standards due to cosmetic imperfections or spoilage can become waste. Finding ways to utilize or manage this type of waste can help reduce losses.

vii. **Wood and Plant Material:** Wood from pruning, clearing, or cutting down trees for agricultural purposes can generate waste. This material can often be used for bioenergy production, mulching, or as a source of raw materials.

1.1 Management of Agricultural Waste

Efforts to manage agricultural waste often involve practices like composting, recycling, biogas production, using waste as animal feed, and integrating waste management plans into overall farm management strategies. Proper management of agricultural waste is important for several reasons:

i. **Environmental Impact:** Poorly managed agricultural waste can lead to soil degradation, water pollution (through runoff and leaching of nutrients and chemicals), and air pollution (due to the release of greenhouse gases from decomposition).

ii. **Resource Efficiency:** Many agricultural wastes contain valuable nutrients and organic matter that can be recycled to improve soil fertility, reduce the need for chemical fertilizers, and enhance crop yields.

iii. **Bioenergy Production:** Certain agricultural wastes, like crop residues and animal manure, can be used to produce biofuels or biogas, contributing to renewable energy generation.

iv. **Circular Economy:** Repurposing agricultural waste for other uses, such as composting, animal feed, or bioplastics, aligns with the principles of a circular economy, minimizing waste and maximizing resource utilization.

v. **Regulatory Compliance:** Many regions have regulations in place to ensure proper disposal and management of agricultural waste to prevent negative environmental impacts.

1.2 Super-capacitors

Super-capacitors, also known as ultracapacitors or electrochemical capacitors, are energy storage devices that can deliver high power quickly and
efficiently[13]. They are used in various applications where rapid energy storage and discharge are required, such as in hybrid vehicles, renewable energy systems, and electronic devices. The performance of a supercapacitor depends largely on the properties of its electrode materials. The high cost of supercapacitors is one of the primary barriers to their widespread adoption. Traditional supercapacitors rely on expensive carbon source materials like coal and fusel fuel activated carbon and graphene, which contribute to their high cost.

1.2.1 Types of Supercapacitors

Supercapacitors make use of two basic principles for energy storage i.e. electrochemical pseudocapacitance and static double-layered capacitance. Based on this, supercapacitors are categorized into three different types[14] as shown in Figure 1 below.

**Figure 1**: Classification of Supercapacitors based on Electrode Materials

i. Electrochemical Double Layered Capacitors (EDLCs)

In Double Layered Capacitors, the Storage of electrical energy is achieved by charge separation in Helmholtz double layer. This acts as a boundary between the conductor electrode and electrolyte. Double-layer capacitors (EDLCs) make use of high surface area carbon materials like activated carbon, carbon nanofibres, carbon aerogels and CNTs.

ii. Pseudocapacitors

They have polymer conducting electrodes or transition metal oxides that possess large electrochemical pseudocapacitance. Storage of electrical energy is an electrochemical process and is achieved through redox reactions and intercalation on the electrode surface by ions that are specifically absorbed.

iii. Hybrid Capacitors

Here, the electrodes are asymmetric where one of the electrodes exhibits electrostatic property while the other exhibits electrochemical capacitance. Because both Pseudocapacitance and Double-Layered capacitance make inseparable contributions to the full capacitance of an electrochemical capacitor. Hybrid capacitors can also have asymmetric electrodes, of which one has electrostatic and the other has electrochemical capacitance.

1.2.2 Supercapacitors Materials

A supercapacitor consists of electrode, electrolyte and separator, where electrode plays a vital role for the performance of supercapacitor[15-17].

**Figure 2**: Cross section of a Supercapacitor’s Assembly

(a) Coin cell assembly (b) Cylindrical cell
It is important to search electrode materials with excellent performance. The properties of supercapacitors are related to the interaction of their materials. Particularly, the combination of electrode material and type of electrolyte determines the functionality and thermal and electrical characteristics of the capacitors.

**i. Electrode**
The capacitance of the device is largely reliant on characteristics of electrode properties.[18]. Electrodes must have the properties as good conductivity, high chemical stability, controlled pore structure, high corrosion resistance, temperature stability, processability, environmentally friendly and low cost [19]. Spongy, porous material can be used as electrode. By porous electrode material having proper structure that matches with the size of the electrolyte ions improves the electrochemical performance. Suitable pore size distribution has greater influence on capacitance, specific energy, equivalent series resistance and specific power.

**ii. Electrolyte**
Electrolyte consists of solvent and dissolved chemicals that separate into positive and negative ions which make the electrolyte electrically conductive. The conductivity is dependent on the number of ions in the electrolyte [20]. The function of electrolyte is to provide the molecules for separating monolayer in Helmholtz double layer and to deliver the ions. The operating voltage, specific capacitance, power density of electrochemical capacitors is greatly influenced by the choice of electrolyte. The thickness of the double layer is dependent on the concentration and ion size of the electrolyte.

**iii. Separator**
The properties of separator also affect the performance of a supercapacitor. A separator physically separates the two electrodes and exclude the electrical contact between them but allows ionic charge transfer. It should have high electrical resistivity, high ionic conductance, very thin, porous to reduce ESR and chemically static to keep the stability and conductivity of electrolyte.

### 1.2.3 Materials for Supercapacitors electrode
The selection of materials for supercapacitors electrode application largely depend on capacitance and charge storage ability of the materials [21, 22].

#### 1.2.3.1 Carbon materials
Carbon materials in any forms are the most used electrode materials for the fabrication of supercapacitors electrode, this is due to their Low cost, high surface area, availability and established electrode production technologies [6, 23]. Examples of carbon materials used as electrode materials are activated carbon, carbon aerogels, carbon nanotubes, graphene etc.

#### 1.2.3.2 Sources of Carbon Materials
Presently, the source of supercapacitors electrode materials is at Commercial level are from coal, lignite, coconut shells and wood peat, thus raising the cost of commercial activated carbon[12, 24].

### 1.2.4 Common Electrode Materials for Supercapacitors
Here are some common electrode materials for supercapacitors [25, 26]:

#### i. Activated Carbon: Activated carbon is the most widely used material in supercapacitor electrodes due to its high surface area, porosity, and electrical conductivity. It is typically used in EDLCs and provides high capacitance by allowing a large number of ions to be stored at its surface.

#### ii. Graphene: Graphene, a single layer of carbon atoms arranged in a two-dimensional lattice, has exceptional
electrical conductivity and surface area. It can be used as both a standalone electrode material and as an additive to improve the performance of other materials.

iii. **Carbon Nanotubes (CNTs):** CNTs are cylindrical nanostructures made of carbon atoms. They possess high electrical conductivity and mechanical strength, making them suitable for supercapacitor electrodes. They can be used as standalone materials or incorporated into composites.

iv. **Transition Metal Oxides:** Transition metal oxides, such as ruthenium oxide (RuO2), manganese oxide (MnO2), and cobalt oxide (Co3O4), are often used in pseudocapacitors. These materials undergo reversible redox reactions, allowing for higher energy density compared to EDLCs.

v. **Conducting Polymers:** Conducting polymers like polyaniline (PANI), polypyrrole (PPy), and poly (3,4-ethylenedioxythiophene) (PEDOT) exhibit both electrical conductivity and redox properties. They are used in pseudocapacitors, offering a balance between capacitive and faradaic behavior.

vi. **Metal Organic Frameworks (MOFs):** MOFs are porous materials composed of metal ions or clusters linked by organic ligands. They have gained attention for supercapacitor applications due to their high surface area and tunable properties.

vii. **MXenes:** MXenes are a class of two-dimensional materials consisting of transition metal carbides, nitrides, or carbonitrides. They exhibit good electrical conductivity and are being explored for various energy storage applications, including supercapacitors.

viii. **Hybrid Materials:** Researchers often combine different materials to create hybrid electrode structures that leverage the strengths of each component. For instance, combining carbon materials with transition metal oxides can provide a synergistic effect for improved performance.

### 2.0 Sustainability of Energy Storage Devices

Sustainability refers to the ability to meet the needs of the present without compromising the ability of future generations to meet their own needs [27, 28]. This involves a careful balance between environmental, social, and economic factors in order to create a long-term, stable system that can endure over time. Sustainable development is an ongoing process that requires cooperation among governments, businesses, and communities to ensure that resources are conserved, waste is minimized, and the well-being of people and the planet is prioritized. Projects and initiatives that prioritize sustainability may include the use of renewable energy sources, the reduction of greenhouse gas emissions, the conservation of natural resources, and the development of more sustainable forms of agricultural, transportation, and housing [29].

Sustainable energy storage refers to the development and use of storage technology that enable the efficient and reliable use of renewable energy resources such as solar, wind, and biomass [30, 31]. These technologies are essential for reducing reliance on fossil fuels and mitigating the negative environmental impacts of traditional energy sources. Examples of sustainable energy storage...
technologies include batteries, pumped hydro storage, compressed air energy storage, flywheels, hydrogen fuel cells, thermal energy storage, and capacitors/supercapacitors. Each technology has varying degrees of efficiency, durability, cost-effectiveness, and environmental impact [11]. Advancements in sustainable energy storage are crucial for maximizing the benefits of renewable energy and accelerate the transition to a low-carbon world. They can help stabilize and balance electricity grids, increase energy availability during peak demands, and reduce greenhouse gas emissions associated with fossil fuel energy production.

3.0 Agricultural Waste as a Source of Electrode Materials for Supercapacitors

It's worth noting that the choice of electrode material depends on the specific requirements of the supercapacitor application, such as energy density, power density, cycle life, and cost [32]. Ongoing research in materials science continues to explore new materials and fabrication techniques to enhance the performance of supercapacitors. Using agricultural waste as a source of electrode materials for supercapacitors is an innovative idea that aligns with both sustainability and cost-effectiveness [33-35]. Agricultural waste, such as crop residues, husks, shells, and other byproducts, can potentially serve as a low-cost and environmentally friendly alternative to traditional electrode materials for supercapacitors.[36]

3.1 Advantages:

i. **Cost-effectiveness:** Agricultural waste is often considered a waste product and can be obtained at relatively low or even no cost. This can significantly reduce the overall material cost of supercapacitor production.

ii. **Sustainability:** Utilizing agricultural waste reduces the environmental impact associated with waste disposal. It also reduces the demand for traditional electrode materials like activated carbon, which might be derived from fossil fuels.

iii. **Renewable source:** Agricultural waste is a renewable resource, making it a more sustainable option compared to materials that are finite or non-renewable.

iv. **Local availability:** Agricultural waste is abundant in agricultural regions, which means that production could potentially be localized, reducing transportation costs.

3.2 Challenges:

i. **Consistency and quality:** Agricultural waste can vary in terms of composition and quality, which might affect the performance and reliability of supercapacitors. Developing standardized processing methods to ensure consistent electrode material properties is crucial.

ii. **Material performance:** Supercapacitor electrode materials require specific properties, such as high surface area, porosity, and conductivity. It's essential to assess whether agricultural waste can meet these requirements and to optimize processing techniques accordingly.

iii. **Processing techniques:** Developing effective and scalable processing techniques to convert agricultural waste into suitable electrode materials can be a challenge. This might involve techniques such as carbonization, activation, and chemical treatment.

iv. **Testing and validation:** Rigorous testing is required to ensure that
supercapacitors using agricultural waste-based electrodes perform adequately in terms of energy storage capacity, cycle life, and other relevant metrics.

### 3.3 Steps to Explore the Concept:
Researchers have developed a process to convert the agricultural waste into porous carbon materials, which can then be used as electrodes in supercapacitors. The carbon materials have high surface area, allowing them to store large amounts of charge [37]. Additionally, the process is environmentally friendly, using only water and heat to convert the waste into the carbon material [34, 37]. The use of agricultural waste for energy storage also has the potential to provide a new source of income for farmers. Instead of burning or disposing of the waste, it can be sold to companies that produces supercapacitors electrode. The use of agricultural waste for supercapacitor electrodes has the potential to be a sustainable and economically viable solution for energy storage [35].

i. **Material Selection:** Identify agricultural waste materials that have the potential to be transformed into suitable electrode materials. This could include rice husks, coconut shells, corn stalks, and more.

ii. **Material Processing:** Develop and optimize processing techniques to convert the agricultural waste into high-quality electrode materials. This might involve carbonization, activation, and other treatments.

iii. **Characterization:** Thoroughly characterize the resulting electrode materials to ensure they meet the necessary properties for effective supercapacitor performance. This includes assessing surface area, porosity, conductivity, and electrochemical behavior.

iv. **Electrode Fabrication:** Develop methods to incorporate the agricultural waste-based electrode materials into supercapacitor structures. This might involve techniques like slurry coating, film casting, or other deposition methods.

v. **Testing and Validation:** Test the fabricated supercapacitors using agricultural waste-based electrodes in real-world conditions. Evaluate their energy storage capacity, cycle stability, and other performance metrics.

vi. **Optimization:** Iteratively refine the processing techniques and electrode fabrication methods based on testing results. Strive to enhance performance and stability while minimizing costs.

vii. **Scale-up and Commercialization:** Once a viable solution is developed and proven, explore the possibilities of scaling up production and commercializing the technology.
### Table 1: Some Successful Agricultural Waste for Super-Capacitors Electrode

<table>
<thead>
<tr>
<th>S/NO.</th>
<th>Agricultural Waste</th>
<th>Surface Area $m^2/g$</th>
<th>Capacitance F/g</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pistachio Shells (Activated Carbon)</td>
<td>933-1742</td>
<td>47 - 122</td>
<td>Chi-Chang Hua, et al. [38]</td>
</tr>
<tr>
<td>2</td>
<td>Cationic starch, Cassava starch, Corn starch and Graft copolymer starch (Activated Carbon)</td>
<td>1330-1510</td>
<td>170 - 200</td>
<td>Li, et al. [39]</td>
</tr>
<tr>
<td>3</td>
<td>Argan (Argania spinosa) seed shells</td>
<td>2100</td>
<td>355</td>
<td>Elmouwahidi, et al. [40]</td>
</tr>
<tr>
<td>4</td>
<td>Wood wastes</td>
<td>129.8</td>
<td>347</td>
<td>Shuai Yu [41]</td>
</tr>
<tr>
<td>5</td>
<td>Gelam wood sawdust (Melaleuca cajuputi Powell)</td>
<td>-</td>
<td>102</td>
<td>Syarif, et al. [42]</td>
</tr>
<tr>
<td>6</td>
<td>Rice husk</td>
<td>1355–3322</td>
<td>179.4</td>
<td>Lili Dinga, et al. [43]</td>
</tr>
<tr>
<td>7</td>
<td>Coconut shell</td>
<td>2440 - 1121</td>
<td>168 - 246</td>
<td>Akshay Jain, et al. [44]</td>
</tr>
<tr>
<td>8</td>
<td>Willow catkins</td>
<td>645</td>
<td>340</td>
<td>Kai Wang, et al. [45]</td>
</tr>
<tr>
<td>9</td>
<td>corncob</td>
<td>3054</td>
<td>401.6</td>
<td>Wang, et al. [46]</td>
</tr>
<tr>
<td>10</td>
<td>Hemp stem (hurd and bast)</td>
<td>2879</td>
<td>160</td>
<td>Sun, et al. [47]</td>
</tr>
<tr>
<td>11</td>
<td>Tobacco waste</td>
<td>1297.6</td>
<td>148</td>
<td>Chen, et al. [48]</td>
</tr>
<tr>
<td>12</td>
<td>Dry corn straw</td>
<td>3237</td>
<td>227</td>
<td>Lu, et al. [49]</td>
</tr>
<tr>
<td>13</td>
<td>Borassus flabellifer flower</td>
<td>633.43</td>
<td>238.2</td>
<td>Sivachidambarama M, et al. [50]</td>
</tr>
<tr>
<td>14</td>
<td>Fructose corn syrup</td>
<td>1473</td>
<td>168</td>
<td>Wenxin and Fuqian [51]</td>
</tr>
<tr>
<td>15</td>
<td>Gunkgo leaf</td>
<td>835.4</td>
<td>374</td>
<td>Xinqiang Zhu, et al. [52]</td>
</tr>
<tr>
<td>16</td>
<td>Pig manure</td>
<td>2335.9</td>
<td>211.5</td>
<td>Zhang, et al. [53]</td>
</tr>
</tbody>
</table>
4.0 Discussion
Agricultural waste can be conveniently used to replace conventional or commercial activated carbon for the production of electrode for supercapacitors application, because the results from the literature compare well with commercial activated carbon with surface area of 758 and 1771 m²/g used for fabrication of electrode for supercapacitors application have a capacitance of 128 and 235 F/g respectively [54]. However, when selecting a biomass for supercapacitors electrode, firstly, consideration must be given to availability, efficient collection and transportation, this is necessary because agricultural waste are often seasonal and may not be available year-round, leading to fluctuations in the supply of the feedstock and potential production delays and also agricultural waste are spread over large areas, making it difficult to collect and transport to production facilities. This can result in high transportation cost and energy consumption. Also precursor materials with lowest moisture content and ash content, this is because biomass with high moisture and ash content increase the energy required for drying and can result in lower quality and yield of the biochar.

Utilizing agricultural waste for supercapacitor electrode materials can contribute to sustainable energy storage solutions and help address the high cost of traditional electrode materials. However, extensive research, development, and collaboration between researchers, engineers, and agricultural experts will be necessary to overcome the challenges and realize the potential benefits of this innovative approach. It is therefore necessary that the future directions on biomass for supercapacitors electrode should focus on searching for new agricultural waste to be utilized as precursor material for electrode production and also new technologies that can synthesizes agricultural waste to activated carbon at a low cost and good/high surface area and yield.

5.0 Conclusion
The electrochemical super capacitors electrode produced from agricultural waste demonstrate the feasibility and potentials of using this waste to produce a low cost electrode and offers promising prospect for the super capacitors industry. Hence, agricultural waste holds great potential as a solution to high cost of supercapacitors. By utilizing these waste materials to develop low-cost carbon-based electrodes, we can reduce the cost of supercapacitors, promote sustainable waste management, and enable wider adoption of supercapacitor technology in various industries.

Disclosure of conflict Interest
The authors have declared that no competing interest exist.

Reference


[50] Sivachidambarama M et al., "Preparation and characterization of activated carbon derived from Borassus flabellifer flower as electrode material for supercapacitor


