Production and Potential of Activated Carbon from Cassava Peels for Remediation of Active Pharmaceutical Ingredients from Wastewater: A Review

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

ABSTRACT

Cassava peels have been recognized as an ecological burden for the society. Their main advantageous application is animal feeding. However, cassava peels, as many lignocellulosic biomass-rich materials, have stimulated new gateways for the production of renewable, low cost and sustainable adsorbents for water treatment applications. This review compiles the work conducted by various researchers over the last few decades on the use of cassava peels to produce activated carbon for adsorption purposes. In this review, the removal of Active pharmaceutical Ingredients (APIs) by activated carbon (AC) form agricultural waste has been reviewed and compared with the accruing properties of Cassava peels. The different production processes that have been employed to develop and improve the activated carbon from cassava peels have also been presented to highlight and discuss the key advancements on the viability of a wider scale production of activated carbon from cassava peels. The factors affecting the removal of APIs using AC have been reviewed. The mechanisms of applying activated carbon from cassava peels to effectively adsorb both organic and inorganic content have been reviewed and possibilities
of further improvement highlighted. The paper also discusses the key research gaps in the area of customizing the production of Activated carbon from cassava peels for abatement of APIs from wastewater.

**Keywords:** Cassava peel; activated carbon; active pharmaceutical ingredients.

### 1. INTRODUCTION

Pharmaceutical based environmental pollution has become an international issue which requires due attention and changes in policies and regulations [1,2]. Pharmaceuticals are synthetic or natural chemicals that can be found in prescription medicines, over-the-counter therapeutic drugs and veterinary drugs. Pharmaceuticals contain active ingredients that have been designed to have pharmacological effects and confer significant benefits to society but can also be hazardous to human, aqua and other biota lives due to uncontrolled exposure to the environment [3]. Pharmaceuticals have been detected in surface water, ground water and the most public concern has been in drinking water [4]. The occurrence of pharmaceuticals in the environment and the water cycle at trace levels in the range of nanograms to low micrograms per litre has been widely discussed and published in literature in the past decade [4-6]. Most of these studies made on pharmaceuticals in the environment have been made in developed countries that have sufficient wastewater treatment [3,7,8] yet these are a structurally diverse class of contaminants globally. The most recent study on the prevalence of eighteen APIs in Lake Victoria-Uganda showed concentrations as high as 5600 ngL\(^{-1}\) [9].

Pharmaceuticals are constructed to leave the body after their effect has been exerted [10]; hence they eventually end up in the wastewater. As a consequence, APIs are constantly released into the environment from treated or untreated wastewater [11]. Some treatment processes can and do reduce the concentrations of pharmaceuticals in water. These include; biodegradation, photolytic degradation, ozone-bio degradation [12], nano-membranes [13] among others. However, the degree of efficacy is often a function of chemical structure [14], cost [15], energy and nature of the bi-product [16].

Adsorption is one of the alternative methods that is highly regarded for remediation of pharmaceuticals from wastewater [10,17–19]. In developed economies, activated carbon is the most widely used adsorbent for waste water treatment because of its extended surface area, micro porous structure, high adsorption capacity and high degree of surface reactivity [20–22]. However, commercially available activated carbons are very expensive. Besides the off-shelf cost, the non-renewable raw materials from which they are produced are a threat to the environment hence limiting their applications in wastewater treatment.

To find alternatives to commercial activated carbon, various research assays into low cost eco-friendly raw materials for activated carbons have been undertaken. Some of the potential raw materials include; pulp mill sludge [6], rice husks [23], walnut shells [24], scrap tires [25], cassava peels [18,26], cassava stem [27]. Other materials have been discussed elsewhere [20,28–35]. One major factor that affects the use of the mentioned raw materials is the availability and ease of preparation of activated carbon from them. Availability determines sustainability for large-scale applications. The Food and Agricultural Organization (FAO) estimates put the global harvest in 2018 at 277 million tons, representing a 60 percent increase since 2000 and an annual growth rate double that of the previous two decades [36]. On average, cassava peels constitute 10% to 15% of the total tuber weight. This implies that an estimated amount of 27.70 to 41.55 million tons of cassava peel were generated. Leveraging the properties of cassava peels for activated carbon is of an economic importance and also provides an alternative to commercial adsorbents deployed in wastewater treatment.

Many scholars have documented the preparation methods of activated carbon from Cassava peels and its application in wastewater treatment. However most of these are concerned with removal of organic matter [21], dyes [37–39] and heavy metals [40]. Pharmaceuticals are quite diverse and their adsorptive characteristics vary across families. More so, the combined effect of APIs co-existing in a medium has been reported as hazardous relative to the individual effects [41]. It is due to such impasses that curbing APIs has necessitated combinatorial approaches.
2. METHODOLOGY

Both review and original research articles from peer-reviewed journals were reviewed. Reports and policy briefs from accredited organizations regarding pharmaceutical occurrences in the environment and mitigation measures were searched and reviewed from a number of sources such as Google scholar, Scopus and publisher-specific search engines especially ScienceDirect, Sciedomain, Springer. The Boolean operator 'AND' was also used to include several key words in a single search. Search terms included APIs characteristics; APIs occurrence in waste water; Occurrence of APIs in the environment; methods of APIs removal from waste water; cassava peel activated carbon; agricultural waste based activated carbon; Factors affecting remediation of APIs from water systems; production of activated carbon; activated carbon from cassava; proximate analysis of cassava peel; ultimate analysis of cassava peels, proximate and ultimate analysis of cassava peel activated carbon. Preparation of activated carbon from cassava peels; waste water treatment methods; Properties of Cassava peel for production of Activated Carbon; Physical activation of carbon; Chemical activation of carbon, Application of activated carbons to remove APIs from wastewater, Factorial analysis of the potential of activated carbons in remediating APIs from water. Some references in the reviewed articles were further explored for more information on the research subject. Most of the papers and articles reviewed were published in the last ten years. There are exceptions where such literature was lean or where a key component of the subject was mentioned in a manuscript published earlier than ten years. The articles reviewed lie in the research areas of Materials science and Engineering, Chemistry, Pharmacy, and water Engineering.

3. GLOBAL CASSAVA PEEL PRODUCTION AND ALTERNATIVE APPLICATIONS

Cassava is a food crop cultivated mainly in the tropics and sub-tropic regions of the world. It is the third largest carbohydrate food source in the tropics after rice and corn [46] and ranked as the fifth most important food crop in the world as shown in Fig. 1(a). The global cassava production in 2018 is estimated at 277 million tons (fresh root equivalent) with Africa contributing more than 50% [47]. In literature volumetric estimates of cassava peel are rare and the availability, supply chain of cassava peels is tied into that of cassava processing. Hence, the volumes of cassava peel based on a 10 -15% tuber weight composition can be estimated from Fig. 1(b).

The commonest current use of cassava peels is animal feed supplement. However, this is limited by the low cassava protein content (<6%) and hence not recommended beyond certain levels in animal feed [48]. The presence of hydrocyanic other toxicants like hydrocyanic acid and tannic acid that are non-nutrients also limits processing
of cassava peels into animal feeds. Besides being used as low value animal feed, cassava peel has a number of industrial applications. Cassava peels are utilized for energy production through thermo-chemical and biochemical processes. Thermochemical processes comprise of combustion, pyrolysis and gasification [49] while biochemical processes comprise of anaerobic digestion [50] and bioethanol fermentation [51]. However, these processes have been reported as uneconomical with the processing technology still at infancy [51]. This therefore poses minimal competition to the synthesis of these peels into bio-adsorbents.

Fig. 1(a). The five most important staple crops (in 2014) in the world and Africa [47]

Fig. 1(b). World cassava production [47]
Table 1. Comparison of physico and biochemical compositions of cassava peel with other potential agricultural waste precursors

<table>
<thead>
<tr>
<th>Agricultural waste</th>
<th>Moisture content (%)</th>
<th>Volatile matter (%)</th>
<th>Ash content (%)</th>
<th>Fixed Carbon content (%)</th>
<th>Lignin</th>
<th>Cellulose</th>
<th>Hemicellulose</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Banana peel&lt;sub&gt;db&lt;/sub&gt;</td>
<td>13.55</td>
<td>86.44</td>
<td>3.85</td>
<td>31.79</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[58]</td>
</tr>
<tr>
<td>Cassava peel&lt;sub&gt;db&lt;/sub&gt;</td>
<td>-</td>
<td>11.38</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[57]</td>
</tr>
<tr>
<td>Cassava peel&lt;sub&gt;db&lt;/sub&gt;</td>
<td>11.4</td>
<td>59.4</td>
<td>0.29 - 0.31</td>
<td>28.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[56]</td>
</tr>
<tr>
<td>Cassava peel&lt;sub&gt;db&lt;/sub&gt;</td>
<td>-</td>
<td>3.7</td>
<td>-</td>
<td>-</td>
<td>10.88</td>
<td>14.17</td>
<td>23.4</td>
<td>[60]</td>
</tr>
<tr>
<td>Apple peel&lt;sub&gt;db&lt;/sub&gt;</td>
<td>6.0 – 12.2</td>
<td>62.96– 92.03</td>
<td>0.5 – 15.35</td>
<td>42.74 – 74.30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[20]</td>
</tr>
<tr>
<td>Walnut shells&lt;sub&gt;db&lt;/sub&gt;</td>
<td>3.4</td>
<td>-</td>
<td>-</td>
<td>46.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[24]</td>
</tr>
<tr>
<td>Green pea peels&lt;sub&gt;db&lt;/sub&gt;</td>
<td>9.39</td>
<td>14.25</td>
<td>5.69</td>
<td>70.67</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[61]</td>
</tr>
<tr>
<td>Coconut shell&lt;sub&gt;db&lt;/sub&gt;</td>
<td>8.86</td>
<td>-</td>
<td>0.56</td>
<td>45.03</td>
<td>33.3</td>
<td>30.58</td>
<td>26.7</td>
<td>[62]</td>
</tr>
</tbody>
</table>

<sup>db</sup> = dry basis composition, <sup>wb</sup> = wet basis composition
4. CASSAVA PEEL PHYSICAL AND BIO-CHEMICAL COMPOSITION AS A PRECURSOR FOR ACTIVATED CARBONS

For a material to be suitable for activated carbon production, the core determinant parameters are surface area, fixed carbon content, ash content, moisture content, pH, residue matter and water-soluble matter [52,53]. Nwoko et al. [54] investigated the bio-composition of three cassava cultivars and his findings reveal that averagely cassava peels have a moisture content ranging from 66.08% to 72.39%, the ash content ranged from 2.90% to 3.25% indicating low mineral contents in the peels. Most proximate and ultimate analyses reported about activated carbons from cassava peels were done on already carbonized and activated peels [55,22]. This is because the intentions were on the AC properties rather than the raw peel composition. Some proximate analyses on cassava peel prior to carbonization show the compositions of cassava peel in weight percentages as: 11-12% for moisture content, 58-62% for volatile matter, 28-30% for fixed carbon and 0.2-0.4% for ash content [56]. The ash content of cassava peel which is lower than 5% weight composition is suitably applicable for activated carbon production [15]. This is further supported by the fact that cassava peels with such ash content may not require alkaline pretreatment to remove ash forming elements [23]. This is not only economical but also eco-friendly since it eliminates potentially hazardous bi-products of alkaline pre-treatment. However, cassava peel ash content values above 5% have been reported elsewhere with ranges 7.0-12.8%. These discrepancies have been attributed to climatic and harvesting season variations [57]. Table 1 summarizes the precursor properties of cassava peels with other agricultural waste that are potential AC precursors.

5. PRELIMINARY PREPARATION OF CASSAVA PEELS

Preliminarily the peels are washed with distilled water to remove any surface dirt and debris [52]. The peels can be dried in sunlight [39] for about 12 to 24 hours (depending on the sun intensity and the peel wetness), using an oven [63] or a combination of the two methods [64]. The core purpose of drying is to reduce the moisture content to about 10-15% wet basis [56,57]; so that heat energy for the subsequent carbonization and activation processes is less spent on extracting the moisture. After drying, the peels are crashed to increase surface area for activation.

6. ACTIVATION OF CASSAVA PEELS

Activation of cassava peels can be done physically or chemically. Some studies have presented effects of combining both methods. This section includes reviews of activating cassava peels under different conditions.

6.1 Physical Activation

Physical activation is a process that produces activated carbon through sequential processes of carbonization and activation using heat energy in an inert atmosphere. The thermal treatment methods involved in physical activation are simple but energy intensive since they normally need high temperatures. Hence, activation by microwave, ultrasound irradiation, plasma treatment, and electrochemical modification methods has recently emerged to improve activated carbon characteristics at reasonable costs [65].

Carbonization is the first step in physical activation. It is carried out in an oxygen-limited environment so as to effect pyrolysis of the carbon species present in the peels. The peels are subjected to temperature ranges of 350 – 850°C for 1-5 hours [55,27]. Carbonization removes the non-carbon species and produces a raw char with a high percentage of carbon. Raw Carbonizing can be done in a nitrogen atmosphere [24]. Some researchers deployed other means of limiting oxygen interference like filling the inner space of the carbonizing container with sand [52]. Carbonizing can be done using different heat sources including but not limited to; Muffle furnaces, microwave and ultrasound irradiation. Microwave assisted pyrolysis is proving more efficient in the recent studies due to shorter process times [16,34,66].

After carbonizing, activation is done at temperature ranges of 400 - 1000°C using steam and carbon dioxide as the main activating agents [24]. The core aim of activating the raw char is to increase the internal surface area via partial gasification of the carbon skeleton. Recent studies show that harnessing the gases from the carbonization process as the activating agent can combine carbonization and activation [24,67,27]. The activation time ranges between 60 – 180 minutes depending on the activation
temperature. Lower temperatures necessitate longer activation time, which is advantageous in terms of enabling larger surface areas for the AC. However this could be uneconomical especially if the activation method involves electric power. Activated carbon prepared by physical activation has relatively less adsorptive capabilities compared to chemically activated carbon [52]. The surface area of physically activated carbon range is 5 - 654 m²/g, which is relatively low compared with the surface areas of chemically activated carbons that can approximately reach 2000 m²/g [68]. Despite the relatively lower surface areas of the resultant ACs, physical activation is opted for in some cases due to its simplicity and less hazardous bi-products compared to chemical activation. The surface area may not be as significant in API removal as with other adsorbates [69], [70]. Contrarily, Mailler et al. [71] correlated API removal well with BET surface area. The more heterogeneous and porous the adsorbent surface is the higher the surface area for the adhering API molecules. The activation time has a significant effect on the surface area. Surface area increases with increase in activation time [27]. This is because exposing the carbonaceous material particles at high temperature for a long time leads to evaporation of the inner parts of the particles and hence deeper pores are created. These pores are pertinent in allowing the large API molecules into the inner surfaces of the absorbent [14]. The suitability of an adsorbent in abating APIs has been correlated well with other parameters (detailed in section 7.1) including $\text{UV}_{254}$ absorbance [72], bulk density [71]. It is therefore pertinent to study the suitability of API removal of cassava peel AC basing on these characteristic parameters.

6.2 Chemical Activation

Chemical activation involves heating the dried peels with an activating reagent at temperature ranges of 200 to 1050°C for 7 - 14 hours [56,63] depending on the activating agent. The heated material is then washed with distilled or deionized water and treated with a neutralizing agent to remove any impurities of the activating agent [52,29]. The resulting AC is then dried preferably in a vacuum furnace at about 100°C [73].

Chemical activation employs a range of activating agents both alkaline [73,22] and acidic [52]. For acidic activation phosphoric acid ($\text{H}_3\text{PO}_4$) is the most used reagent [74] whereas alkaline agents include $\text{ZnCl}_2$ [75], NaOH and KOH [63,76]. Recent innovative studies have combined NaOH and KOH [77,78] Alkaline activation remains better at producing robust AC in terms of yield, BET surface area and mesopore volume. Liou. [79] reported mesopore volumes as high as 1.07 and 0.95 cm³/g, and mesopore contents of 81.2 and 74.0%, for $\text{ZnCl}_2$ and $\text{H}_3\text{PO}_4$ respectively for ACs produced from sugar cane bagasse and sunflower seed hull.

The characteristics of cassava peel activated carbon produced by chemical activation are more superior compared to those activated physically. Surface area (m²/g) range is 490 - 1605 [52,56,73]. Temperature is a key parameter during chemical activation. Increasing temperatures accelerates volatilization hence giving way for existing pore development and creation of new ones. Impregnation ratio of activating reagent (g) to the mass of the cassava peal (always expressed, as weight percentages (wt%)) are critical in determining the characteristics of chemically activated cassava peel carbon. Various researchers have studied the effect of impregnation ratios at a fixed temperature. Studies involving KOH as the impregnating reagent show that activated carbon yield decreases with increasing impregnation ratio of reagent to cassava peel (mass basis) from 1:2 to 5:2. This is because the surface weight of carbon reduces with increasing KOH owing to the gasification of surface carbon accelerated by the oxidation tendency of KOH. The BET surface area and pore volumes increase with increase in impregnating agent to carbon ratio [56]. Moreover increasing the impregnation ratio increased the tendency of pore enlargement to mesopores that is crucial in adsorbing large molecules of APIs [14]. Generally, conventional activated carbons have a mesopore volumes in the range of 0.1 – 0.5 cm³/g [80,81]. This is because their applications are more biased to micropore volumes rather than Mesopores. In a study of the porous structure of phosphorous acid activated carbon from Corn, the BET surface area and all pore volumes (total, micropore and mesopore) increased with increasing ratio of impregnation (H₃PO₄: dry corn mass) up to 1.0 [82]. With process modifications and robust controls, mesopore volumes of chemically ACs have been reported to surpass 1.0 cm³/g [79,83]. Base-leaching the precursor prior to activation can enhance such mesoporosity by enlarging the micropore structure of the resulting carbon during the subsequent activation processes [79].
6.3 Comparative Analysis of Physical and Chemical Activation

Comparative studies have shown that chemical activation has a higher efficiency based on the proximate analysis values of the surface area [73], decolorizing power and fixed residue [52]. Rajeshwarisivaraj et al. [52] reported 100% quantitative removal of dyes and metal ions by chemically activated cassava peel carbon. This was due to introduction of phosphates due to Phosphoric acid used in the activation process. Sun & Webley, [78] reported a surface area of 3012 m²/g for corncob AC produced through a two-step KOH activation process that is way higher than peak values reported through physical activation.

For the production of AC that is suitable for adsorbing APIs, chemical activation is preferred. This is because mesopore volumes can be improved easily by increasing the activation ratio of the activating agent to the peels [73]. The higher the mesopore volume the better is the adsorptivity [14]. Chemicals favor the elimination of oxygen and hydrogen instead of eliminating carbon oxides and hydrocarbons. This implies a higher loss of volatile mater and better yields of fixed carbon [81].

Pyrolysis temperature has a significant effect on pore structure and therefore surface area for both physical and chemical activation whereas activation time does not affect the pore nexus of chemically activated carbon [56]. In other studies a combinatorial activation process involving further treatment of already physically activated carbon with hydrochloric acid produced fairly better mesopore volumes [84]. Despite the robust adsorptive properties of chemically activated carbon, chemical activation poses a challenge of recovering residual chemicals from the carbon [79].

6.4 Comparative Analysis of Adsorptive Properties of Cassava Peel Activated Carbon with Other Raw Material Developed Activated Carbon

Activated carbon from cassava peels has textural properties like BET surface area and mesopore volume that are similar to, or even better than those exhibited by other source-derived activated carbons, including the commercial activated carbons. Some of these properties are highly dependent on the activation method and the specific conditions during activation. It is therefore pertinent to have a good selection of the activation method coupled with a high level of condition specificity in the activation process. Conventionally, most applications of AC are favored by microporous structures [68]. However, the rise in the number of applications that harness the mesoporous structure has shifted the attention due to wide range of pore sizes and high pore volume. Unlike many adsorbates, APIs have large molecules that are better physically adsorbed by mesoporous adsorbents [14]. Table 2 shows the larger the mesopore volumes the lower the corresponding micropore volumes of ACs. The task is to enlarge micropores of the carbon so that more than 50% mesopores prevail in the resultant AC [85].

6.5 Powdered vs. Granular AC: Production Processes and Applications

The American Society for Testing and Materials (ASTM) classifies particles passing through an 80-mesh sieve (0.177 mm) and smaller as powdered activated carbon (PAC) and bigger as granular activated carbon (GAC) [99]. However, PAC used in practice for water purification has particle sizes of <100 µm and granular activated carbon (GAC) >800 µm [71] with an intermittent class of micro granular activated carbon in the sizes of 200 - 600 µm [14]. The production processes of both powdered and granular ACs do not differ by much. The difference is in the preliminary preparation in which the particle sizes for the powdered type is reduced to micron and submicron particle sizes by milling coal based GAC, using tools like, pulverizers, bead mills and ball mills [100] whereas with granular activated carbon such milling precision is unnecessary.

Powdered activated carbon has a number of applications including; decolorizing liquids [101], natural organic matter removal [102], removal of APIs [103] and synthesis of battery electrodes [104] among others. However, some studies have shown that micro-milling PAC reduces adsorption capacity. This is due to oxidative processes occurring on the surface [105] and the introduction of oxygen/hydrogen -containing functional groups on the carbon surface from water [106].
Table 2. Textural properties of cassava peel AC compared with other sources derived AC

<table>
<thead>
<tr>
<th>Precursor name</th>
<th>Activation process conditions</th>
<th>Textural properties of activated carbon</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Activation Agent</td>
<td>Temperature (°C)</td>
<td>Time (min)</td>
</tr>
<tr>
<td>Banana peel</td>
<td>KOH</td>
<td>500</td>
<td>30</td>
</tr>
<tr>
<td>Rice husks</td>
<td>K₂CO₃</td>
<td>950</td>
<td>60</td>
</tr>
<tr>
<td>Rice husks</td>
<td>KOH (mw)</td>
<td>700</td>
<td>3</td>
</tr>
<tr>
<td>Corn</td>
<td>H₃PO₄</td>
<td>400</td>
<td>60</td>
</tr>
<tr>
<td>Cassava peel</td>
<td>KOH</td>
<td>750</td>
<td>60</td>
</tr>
<tr>
<td>Cassava peel</td>
<td>ZnCl₂</td>
<td>700</td>
<td>30</td>
</tr>
<tr>
<td>Cassava peel</td>
<td>ZnCl₂</td>
<td>200</td>
<td>30</td>
</tr>
<tr>
<td>Cassava peel</td>
<td>ZnCl₂</td>
<td>550</td>
<td>-</td>
</tr>
<tr>
<td>Apple peel</td>
<td>H₃PO₄ (mw)</td>
<td>1000</td>
<td>5</td>
</tr>
<tr>
<td>Orange peel</td>
<td>KOH</td>
<td>700</td>
<td>60</td>
</tr>
<tr>
<td>Walnut shells</td>
<td>K₂CO₃</td>
<td>900</td>
<td>60</td>
</tr>
<tr>
<td>Garlic peels</td>
<td>KOH</td>
<td>850</td>
<td>120</td>
</tr>
<tr>
<td>Pine saw dust</td>
<td>ZnCl₂</td>
<td>500</td>
<td>60</td>
</tr>
<tr>
<td>Corn cob</td>
<td>H₃PO₄</td>
<td>400</td>
<td>-</td>
</tr>
<tr>
<td>Ion exchange resin</td>
<td>Steam</td>
<td>900</td>
<td>1200</td>
</tr>
<tr>
<td>Palm nut shells</td>
<td>Ferrocene (Mw)</td>
<td>600</td>
<td>1800</td>
</tr>
<tr>
<td>Waste palm shell</td>
<td>Steam (Mw)</td>
<td>700</td>
<td>25</td>
</tr>
<tr>
<td>Commercial activated carbon</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Commercial activated carbon</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Persian iron wood</td>
<td>KOH</td>
<td>600</td>
<td>-</td>
</tr>
<tr>
<td>Grape stalk</td>
<td>H₃PO₄</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Mw represents microwave assisted hence power is considered instead of temperature*
Table 3. Production costs of AC from agricultural waste precursors

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Activation agent</th>
<th>Type of AC</th>
<th>Country</th>
<th>Cost of production (US$ per kg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron wood</td>
<td>KOH</td>
<td>Powder</td>
<td>Iran</td>
<td>1.65</td>
<td>[68]</td>
</tr>
<tr>
<td>Iron wood</td>
<td>H$_3$PO$_4$</td>
<td>Powder</td>
<td>Iran</td>
<td>1.58</td>
<td>[68]</td>
</tr>
<tr>
<td>Wheat bran</td>
<td>NaOH</td>
<td>-</td>
<td>China</td>
<td>3.38 – 3.74</td>
<td>[112]</td>
</tr>
<tr>
<td>Cassava peel</td>
<td>-</td>
<td>-</td>
<td>Malaysia</td>
<td>0.71</td>
<td>[95]</td>
</tr>
<tr>
<td>Waste palm shell</td>
<td>Steam</td>
<td>-</td>
<td>Malaysia</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Rice husk</td>
<td>NaOH</td>
<td>Granular</td>
<td>China</td>
<td>3.58 – 3.77</td>
<td>[113]</td>
</tr>
<tr>
<td>Commercial AC (coconut)</td>
<td>-</td>
<td>Granular</td>
<td>USA</td>
<td>9.0</td>
<td>[115]</td>
</tr>
<tr>
<td>Activated carbon (Commercial type Filtrasorb-400)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>20-22</td>
<td>[115]</td>
</tr>
<tr>
<td>Sugar cane bagasse</td>
<td>Steam</td>
<td>Granular</td>
<td>-</td>
<td>3.12</td>
<td></td>
</tr>
<tr>
<td>Coconut shell</td>
<td></td>
<td>Granular</td>
<td>Spain</td>
<td>3.04</td>
<td>[43]</td>
</tr>
</tbody>
</table>

Like PAC, GAC has a number of applications including API adsorption [107]. This is because GAC of various pore sizes can be produced and suitably customized for a particular purpose [107]. The particle size range for GAC has been quoted in many manuscripts as 0.5 - 4.0 mm [108]. In some studies the GAC particle size is way smaller especially for gas adsorption applications. The advantages of GAC over PAC in water treatment systems include: no leakages that would necessitate addition of coagulants like FeCl$_3$, better ability to reduce solid waste and overall simplicity of use for relatively similar costs as PAC [71] among others. GAC can be regenerated and reactivated and hence reduces treatment costs [70,109] though reactivation reduces its quality by blocking some of the pores. However, GAC could require more contact time for API adsorption compared with PAC [110]. This implies that deeper systems are required in case GAC is to be used so as to increase contact time.

6.6 Production Costs of Cassava Peel Activated Carbon versus Other Activated Carbons

The price of biomass-based activated carbon on the world market is averagely US$ 2.2 – 5.0 per kg and varies with the AC quality [111]. There are a number of factors that determine the production cost of activated carbons. Some are direct and others are indirect. The direct costs of production accrue to the processes and equipment used; including the availability of the precursor while the indirect are auxiliary to the core production procedures. As mentioned earlier in section 1, cassava peels are available in many settings in Africa, Asia and the Caribbean owing to cassava being a staple food. Mainly, the costs of production of AC from cassava peels are with the process conditions like carbonizing, activating and some modifications as reported by scholars. The other costs include labor, transportation, sorting, cleaning and more pertinently the geographical location/context that dictates most of the mentioned factors basing on the political and economic situation in a particular location. As reflected in Table 3, no study has been made on the production cost of AC from cassava peels.

7. MECHANISM OF APIs REMOVAL FROM WASTEWATER BY ACTIVATED CARBONS

Most APIs possess aromatic rings that are electron donors. The structure of ACs consists of disorganized graphite sheets with $\pi-\pi$ interlinkages. These linkages act as $\pi$-acceptors [116]. Other active surface groups in ACs effect adsorption through other bonding types like H-bonds which could be Yoshida and or dipole-dipole [117]. This electron donor $\pi$-acceptor relationship is responsible for the adsorption of APIs from wastewater. Besides the electrostatic interactions and other bonding mechanisms, hydrophobicity plays a key role in adsorptivity of APIs. In a study conducted by Margot et al. [118] on comparing AC and ozone in abating over 70
APIs, the most hydrophilic APIs were being eliminated to a lesser extent by AC. The pore filling of the ACs is another mechanism by which APIs are removed from waste water by ACs [117]. Owing to the large molecular sizes of APIs mesopores are preferred to micropores for adsorption of APIs [14]. The larger the mesopore volume compared to micropore volume the higher the adsorption capability of an AC on APIs [117,119].

8. CORE FACTORS AFFECTING REMOVAL OF APIs FROM WASTEWATER USING ACTIVATED CARBON

Quite few studies in literature have tried to establish the core characteristics that accrue to the adsorptivity of pharmaceuticals by ACs. Many of the studies just report how particular ACs fair in removing APIs under particular conditions but do not correlate the removal capacities with the common AC characteristic numbers like B.E.T area, iodine number, methylene blue number and others [5,6,120]. Alves et al. [14] attributed to the large molecular sizes of APIs whose physical adsorption is favored by the mesoporous textural parameters rather than the total pore volumes upon which numbers like BET surface area are based. Some of the studies are presented in Table 4. The properties and mechanisms regarding the adsorptive action of ACs on pharmaceuticals remain unclear.

8.1 Adsorbent (AC) Characteristics

High surface area and porosity development are key aspects in adsorption of organic compounds from wastewater [18,21] yet these are denounced as un necessary by many scholars for adsorption of pharmaceuticals. Zietzschmann et al. [69] reported that both B.E.T surface area and iodine number were generally poor indicators for removal of pharmaceuticals from wastewater. This was backed in a later study on powdered activated carbon (PAC) by Benstoem & Pinnekamp [70] in which B.E.T and iodine number were insignificant parameters in removing pharmaceuticals from waste water treatment plants. However, Mailler et al. [129] found some correlation of B.E.T surface area with adsorptivity and Reza et al. [34] also argued that adsorbent surface topography is key in determining its adsorption capacity on APIs. This is because the more heterogeneous and porous the adsorbent surface is the higher the surface area for the adhering API molecules. Zietzschmann et al. [69] hypothetically concluded that nitrobenzene number could be useful only in predicting the efficiency of PAC in remediating pollutants in cases where the organic micro pollutants have structural similarities with nitrobenzene.

However, UVA$_{254}$ absorption is a handy indicator in approximating the removal of organic micro pollutants like APIs from waste water and hence can be based on when choosing a particular carbon for API remediation [69,71]. Another carbon characteristic number that can be reliably based on when choosing an AC is the density of the AC [70]. The density of granular activated carbons (GAC) showed the highest correlation to the adsorption of three pharmaeuticals, that is $R^2 = 0.91 \pm 0.06$. The other characteristic numbers were not suitable markers for the choice of a particular GAC. Granular activated carbons with lower densities are suitable for APIs removal as long as a robust activation process aimed at yielding large pores is appropriated. De Gisi et al. [15] presented the bulk density ranges of micro, meso and macro porous AC classes as <0.85 cm$^3$/g, 085-1.0 cm$^3$/g and >1.0 cm$^3$/g respectively. For APIs adsorbents, 0.85-1.0 cm$^3$/g is a characteristically suitable bulk density. It is pertinent therefore to consider the density of the carbon, the pore diameter and the UVA$_{254}$ adsorption capacity as key factors that can affect the removal of APIs from wastewater using AC. On a minor, the activation process is worth considering. Alves et al. [14] reported a better global removal (78.6 - 88.5%) of pharmaceuticals using chemically activated micro grain activated carbon (μGAC) at doses of 20 mgL$^{-1}$ compared to 10.5 - 51.4% removal for steam activated μGAC with the same doses. It is evident in the same study that chemically activated μGACs presented a high pore volume with a higher distribution of mesopores which are key in APIs adsorption especially with no background organic matter. The mesopores are more so important since most pharmaceutical molecules are quite large and cannot be accomodated in micropores. The active surface group present in an AC also determines its adsorptive capacity especially with effluent water which has high amounts of background organic matter. Alves et al. [14] concluded that the presence of surface oxygenated groups in an AC could be influential in treating effluent wastewater with positively charged APIs. This is because positive API molecules with loose electrons can easily get electrons from the oxygenated groups and hence
Table 4. Conditions and adsorption capacities of various agricultural waste based ACs for APIs

<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>API removed</th>
<th>Adsorbent dose (gL⁻¹)</th>
<th>Initial API concentration (mgL⁻¹)</th>
<th>Contact time (min)</th>
<th>Temperature (°C)</th>
<th>pH</th>
<th>Adsorption capacity (mgg⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice husk</td>
<td>Ibuprofen</td>
<td>0.3 - 20</td>
<td>100</td>
<td>240</td>
<td>30</td>
<td>-</td>
<td>239.8</td>
<td>[19]</td>
</tr>
<tr>
<td>Rice husk</td>
<td>Tetracycline</td>
<td>5.0</td>
<td>50 - 100</td>
<td>30</td>
<td>-</td>
<td>5-9</td>
<td>16.95 -58.8</td>
<td>[121]</td>
</tr>
<tr>
<td>Walnut shells</td>
<td>Metronidazole</td>
<td>-</td>
<td>40</td>
<td>-</td>
<td>30</td>
<td>8.0</td>
<td>106.9</td>
<td>[89]</td>
</tr>
<tr>
<td></td>
<td>Sulfamethoxazole</td>
<td>-</td>
<td>40</td>
<td>-</td>
<td>30</td>
<td>5.5</td>
<td>16.95 -58.8</td>
<td></td>
</tr>
<tr>
<td>Grape stalk</td>
<td>Caffeine</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>-</td>
<td>4.0</td>
<td>916.7</td>
<td>[98]</td>
</tr>
<tr>
<td>Apple tree branches</td>
<td>Atenolol</td>
<td>-</td>
<td>-</td>
<td>360</td>
<td>30</td>
<td>-</td>
<td>346 - 556</td>
<td>[122]</td>
</tr>
<tr>
<td>Palm Kernel shell</td>
<td>Carbamazepine</td>
<td>1.0</td>
<td>-</td>
<td>240</td>
<td>25</td>
<td>3.0 - 10</td>
<td>0.72ᵇ</td>
<td>[123]</td>
</tr>
<tr>
<td></td>
<td>Atenolol</td>
<td>1.0</td>
<td>-</td>
<td>240</td>
<td>25</td>
<td>3.0 - 10</td>
<td>0.69ᵇ</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acebutolol</td>
<td>1.0</td>
<td>-</td>
<td>240</td>
<td>25</td>
<td>3.0 - 10</td>
<td>0.67ᵇ</td>
<td></td>
</tr>
<tr>
<td>Coffee waste</td>
<td>Sulfamethoxazole</td>
<td>50</td>
<td>100 - 400</td>
<td>1440</td>
<td>25</td>
<td>-</td>
<td>256</td>
<td>[124]</td>
</tr>
<tr>
<td>(sulfonated)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potato peels</td>
<td>Dorzolamide</td>
<td>1.0</td>
<td>0 - 200</td>
<td>-</td>
<td>25 - 65</td>
<td>2.0 - 12</td>
<td>60</td>
<td>[125]</td>
</tr>
<tr>
<td>Date palm leaflets</td>
<td>Ciprofloxacin</td>
<td>2.0</td>
<td>100</td>
<td>-</td>
<td>25 - 45</td>
<td>6.0</td>
<td>125 - 133.3</td>
<td>[33]</td>
</tr>
<tr>
<td>Cork powder</td>
<td>Ibuprofen</td>
<td>0.67</td>
<td>20 - 120</td>
<td>-</td>
<td>25 - 40</td>
<td>2.0 - 11</td>
<td>378</td>
<td>[126]</td>
</tr>
<tr>
<td>Tea waste</td>
<td>Sulfamethazine</td>
<td>1.0</td>
<td>0 - 50</td>
<td>-</td>
<td>25</td>
<td>3.0 - 9.0</td>
<td>33.81</td>
<td>[127]</td>
</tr>
<tr>
<td>Cocoa shell</td>
<td>Diclofenac</td>
<td>2.5</td>
<td>10 - 300</td>
<td>25 - 50</td>
<td>7.0 - 10</td>
<td>-</td>
<td>74.81</td>
<td>[128]</td>
</tr>
<tr>
<td>Bamboo waste</td>
<td>Ibuprofen</td>
<td>1.0</td>
<td>0 - 50</td>
<td>-</td>
<td>25</td>
<td>3.0 - 9.0</td>
<td>278.5</td>
<td>[34]</td>
</tr>
<tr>
<td>Spent mushroom substrate</td>
<td>Sulfamethoxazole</td>
<td>2.0</td>
<td>0.5 - 10</td>
<td>-</td>
<td>-</td>
<td>1.0 - 11</td>
<td>2.2133</td>
<td>[35]</td>
</tr>
</tbody>
</table>

ᵃ = percentage removal of the adsorbate, ᵇ = Adsorption capacity in mmol/g, ᶜ = Adsorptivity based on Freundlich model, (Lmg⁻¹)ⁿ
increasing the electrostatic attraction. Kurniawan et al. [26] reported carboxyl and hydroxyl groups as the active surface groups in cassava peel. With these groups both positive and negative APIs can be abated with adsorptivity dependent on which of the groups is predominant.

8.2 Characteristics of Pharmaceuticals

The molecular charge of a pharmaceutical is a key factor in its removal from wastewater. Pharmaceuticals with positively charged molecules have been found better removed compared to the neutral and negatively charged [129]. This is because the activated carbon groups, having a negative charge, shall have a high electrostatic force onto the positive charges. This is in agreement with Margot et al. [118] who argued that background organic matter that is negatively charged can contribute to the adsorption of APIs by increasing the negative charge of the activated carbon which in turn increases the electrostatic attraction of the positive compounds. Besides the molecular charge, the molecular mass of a particular pharmaceutical is key in its removal. Most of the APIs are large molecules and hence may not be efficiently removed from wastewater if the pores of the AC cannot accommodate them. Another functional characteristic that contributes to removal efficiency is the functional group structure in the pharmaceutical. Aromatic and heterocyclic compounds have been reported to be removed more efficiently from wastewater compared to those that have relatively less number of heterocycles [130].

8.3 Diversity of Pharmaceuticals

The occurrence of a wide range of pharmaceuticals with various properties is another factor that affects their removal. In some studies, other competing APIs with closely similar properties have impeded the removal of targeted APIs. This mainly emanates from the active groups that are quite similar to the targeted APIs. Even then, the presence of APIs with different functional groups requires particular adsorbents that may not be available or cost ineffective. This has therefore called for combinations of various mechanisms in wastewater treatment systems with different adsorptive capabilities so as to curb a wider range of APIs. An example of such a set-up is in a study conducted by Kovalova et al. [131] in which three different mechanisms (AC, ozone and UV light) were deployed to curb 56 pharmaceuticals. It clearly shows that some pharmaceuticals were recalcitrant to both AC and ozone and could predictably be remediated by higher UV dosages. Moreover some APIs are persistent even over long term treatments for some remediation methods [45].

8.4 Quality/Composition of the Waste Water

The quality of the effluent/wastewater being treated is a key factor that affects the removal of APIs. Most of the wastewater contains background organic matter and dissolved organic carbon. In some studies, the presence of organic matter has been proved to be a key factor in the removal of APIs from wastewater [14,129]. Presence of background organic matter creates adsorption competition with the intended APIs and may also block the AC pores [130]. The presence of total suspended solids does not only affect the life span of the adsorbent but also the operability of the remediation systems [43]. It is therefore pertinent that the robust adsorbents for APIs be applied after the conventional wastewater treatment processes capable of remediating organic matter to have more APIs adsorbed. The pH of the waste water is another factor that affects the removal of APIs from wastewater. The adsorption kinetics of APIs increase with lower pH [132]. More review on pH effects is in section 7.7.

8.5 Temperature

Some adsorption kinetics on APIs have shown an increase in adsorption with rise in temperature [33,133]. This is due to the tendency of the AC to expand and letting more active sites free for adsorption [119]. A reduction in adsorptivity has been reported in other studies. In a study conducted by Reza et al. [34] on the adsorptive behaviour of ibuprofen and clofibric acid onto microwave assisted activated bamboo waste, the adsorption of both ibuprofen and clofibric acid reduced with increase in temperature. This indicates that the adsorption process in this study was exothermic and to an extent spontaneous. The spontaneous processes are an indication for a high affinity of the adsorbent towards the adsorbate [119]. It is therefore pertinent to note that some kinetics involved in adsorption of APIs may be spontaneous and may require no external heat source where as others may require.
8.6 Contact Time

Like with other adsorption processes, API adsorption is time dependent. The longer the contact time the higher the adsorptivity [34]. This is due to ample time for the diffusion of APIs to the adsorbent surface. Contact time in many studies has been studied with the equilibrium (when the adsorption rate is constant) as the termination point. Although in practice this seems to be a single process, kinetically it is step-wise and there are critical stages that determine the longevity and effectiveness of the entire process. Physical adsorption occurs with in a short time whereas chemical adsorption takes a relatively longer time. Generally the contact/equilibrium time varies with the adsorbent and adsorbate characteristics like the adsorbate charge, adsorbent porosity, temperature and presence of competing adsorbates among others.

8.7 pH

pH is a key factor in the adsorption kinetics of APIs since it influences the surface charge of the AC and also causes adsorbate ionization [14]. Generally, the adsorption capacity of ACs is inversely related to the pH of the system. Kyzas & Deliyanni, [125] reported that the optimum pH of adsorption of dorzolamide by potato peel based AC was inversely proportional to AC adsorption capacity. This is in agreement with the findings Guedidi et al. [132] in which the adsorption capacity of APIs hiking with lower pH of the aqueous solution. [117] also observed that increasing pH reduced the adsorption capacity of the adsorbent on 5 APIs except for Carbamazepine (where it remained unchanged/slightly increased), and this effect was more obvious when the pH became alkaline. In another study by Spessato et al. [134], the highest and lowest adsorption capacities of paracetamol by super activated carbon (SAC) prepared from biomass were achieved at pH 3.0 -5.0 and 10.0 respectively. The effect of pH on the adsorption of APIs by AC has been discussed more in other studies [98,122,123,127,135,136]. When the solution pH is greater than the point of zero charge (PZC) pH, the AC surface is negatively charged leading to deprotonation of the API rendering it negatively charged [34,118]. The repulsion between the negative charges accounts for the reduction in adsorption capacity. It is therefore pertinent to keep the pH of the solution at levels lower than the point of zero charge value for a particular adsorbate for better adsorption capacities.

9. OTHER ECO-FRIENDLY MECHANISMS FOR REMOVAL OF APIs FROM WASTEWATER

Besides adsorption, other environmentally friendly mechanisms have been reported and have been quite successful in remediating APIs though with some factors impeding their large-scale application as discussed in section 1. These include Photolytic oxidation, biodegradation, ozone biodegradation, and membrane filtration, phytoremediation among others. In some studies a couple of these methods have been deployed in series and considerable improvements in removal efficiencies have been achieved [42,131]. De Wilt et al. [12] applied ozone in between two biodegradation processes and removed 8 out of 9 target pharmaceuticals more efficiently and at a relatively lower cost to the individual processes. Membrane filtration processes like nano-filtration and reverse osmosis are picking momentum in remediating APIs [5]. Others like ultrafiltration and microfiltration still have limitations regarding the pore sizes that let some APIs through due to large diameters [136]. Besides, the competition of background organic carbon with APIs remains a key limitation in deploying some of these mechanisms as stand-alone systems. In the same regard ultra and micro filtrations have been integrated in systems with other methods including adsorption. Sbardella et al. [137] reported 22- 35% contribution to the overall percentage removal of pharmaceuticals by the biological activity of the biofilm that developed on the GAC. Also, biofiltration has been reported as an efficient method when combined with ozone owing to its ability to mitigate any oxidation related bi-products from ozonation [138]. Conventional biodegradation has not successfully remediated APIs with most studies reporting average removal capacities of 50% [118]. Both aerobic and anaerobic wastewater treatment have proved to remediate some pharmaceuticals in wastewater. However there are some APIs that are totally persistent to both of these treatments. Falås et al. [45] investigated the removal of 31 APIs in biological reactors through short and long-term experiments. The study showed that several APIs could be abated by aerobic treatments whereas others like venlafaxine and tramadol were persistent and were removed in anaerobic treatment. Phytoremediation has also proved feasible in curbing APIs in wastewater. A review by Verlicchi & Zambello, [139] showed comparable efficiencies of constructed wetlands in abating a
wide range APIs including all over the counter compounds widely consumed.

10. APIs ADSORPTION BY CASSAVA PEEL ACTIVATED CARBON

From Table 2, the adsorptive properties of various precursors based ACs can be fairly compared with those of cassava peels. Even other non-agricultural waste based ACs compare fairly with cassava peel ACs [6]. It is however inconclusive basing on these properties on whether cassava peel is suitable precursor for AC with ability to remediate APIs. This is because all the adsorptive properties presented in these studies are based on other adsorbates not related to APIs. The core factors presented in section 8 should be further investigated in the case of cassava peel to draw vivid conclusions. Sections 9.1 and 9.2 give comparisons on suitability of powdered and granular AC forms.

10.1 Powdered Activated Carbon

The particle diameter of powdered activated carbon (PAC) ranges between 10 -100 μm. PAC has been applied in removal of APIs and has been quite successful [69,118,129]. However, there is no literature on the adsorption of APIs by cassava peel based (PAC). The most recent study that can be related to other studies on API remediation by other adsorbents is by Parvathi, Shoba, Prakash, & Sivamani, [140]. The dyes studied are the closest cohort of micro-pollutants that can be related to the commonest APIs discussed in literature. This requires further study to affirm this. Despite the fact that PAC has been applied in remediating APIs, it should be noted that super fine PAC milled to micron or submicron sizes presents a disadvantage of introducing oxygen/hydrogen containing functional groups on the carbon surface from the wastewater [106]. It is therefore pertinent to have PAC in the mesopore range as recommended by Alves et al. [14].

10.2 Granular Activated Carbon

Granular activated carbon (GAC) has been applied in the removal of APIs [14,70,141]. However, like for PAC, no literature is available pertaining the application of cassava peel based GAC in abating pharmaceuticals in wastewater. GAC from other agricultural waste materials has been studied in remediating APIs (Parredes et al., 2018). Like most ACs the efficiency and lifetime of GAC depends on a number of factors including the wastewater quality, the precursor type and the carbonization-activation process. GAC can be reactivated and hence reduces treatment costs [70] though reactivation reduces its quality by blocking some of the pores. Some special forms of GAC are re-agglomerated from PAC. All of these factors influence the internal grain structure, as well as the size and the physico-chemical properties of the inner surface. Hatt, Germain, & Judd, [142] reported a lower carbon usage rate for organic matter for GAC compared to PAC for removal percentages above 60%. The same study also showed 80% turbidity removal for all the GACs used. This, coupled with organic matter removal shows that GAC is better in water treatment systems though for micro pollutants it fairs as well as PAC [42,71] as further shown in Table 5. However, GACs should be applied to augment treatment methods that are capable of removing almost all total suspended solids (TSS) such as flocculation filtration and floating bed denitrification. This is due to the tendency of GAC grains to retain some particles. Particle retention necessitates regular back washing leading to abrasion [143,42]. Mailler et al. [71] reported 50 to >90% removal of pharmaceuticals and hormones from waste water using μGAC carbon. In the same study total suspended solids were eliminated possibly due to relatively smaller pores that could have reduced clogging as reported by Altmann et al. [42]. This implies that GAC could be applicable in remediating APIs from raw water with TSS and other organic matter like DOC depending on the average pore sizes.

10.3 Adsorption Isotherms

To explain the adsorption of APIs by various ACs, Langmuir and Freundlich isotherms are the most popularly applied [42,116,119,125] and hence are more detailed in this section. Other isotherms include Dubinin-Radushkevich [117], Liu [134], Temkin, Redlich Peterson and Sips [146] among others. All the adsorption isotherms are generated by plotting the amount of APIs left in solution and the amount of the compound that is on the surface of the adsorbent. At equilibrium, the amount of adsorbate on the adsorbent at equilibrium (mg/g), qe, can be calculated using the balance Eq 1.

\[ q_e = \frac{(C_0 - C_e)V}{W}, \]  

(1)

Where \( C_0 \) (mg L\(^{-1}\)) is the initial liquid-phase concentration of pharmaceutical, \( C_e \) (mg L\(^{-1}\)) is the liquid-phase concentration of pharmaceutical
11. FUTURE PROSPECTS

Literature reveals that APIs still remain a challenging class of micro pollutants both in wastewater and conventionally treated water used in day-to-day lives. Their persistence in water systems and adversity even at nano concentrations is of concern. Pyrolysis assisted chemical activation remains preferred to physical activation owing to better adsorptive properties of the AC produced by chemical activation. Unlike with other adsorbates whose adsorption is determined by characteristic numbers that cut across all adsorbents like BET surface area, pore volume, iodine number, the removal of APIs is dependent on the adsorbent bulk density, pore diameter and UVA_254 adsorption capacity. Literature also reveals that it is more effective to

<table>
<thead>
<tr>
<th>AC type</th>
<th>Grain diameter (μm)</th>
<th>Pore type</th>
<th>Pore diameter</th>
<th>AC dose (mgL⁻¹)</th>
<th>API</th>
<th>Removal efficiency (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granular</td>
<td>-</td>
<td>Micro</td>
<td>0.1</td>
<td>-</td>
<td>Carbamazepine</td>
<td>&gt; 80</td>
<td>[43]</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td>Venlafaxine</td>
<td>76</td>
<td>[14]</td>
</tr>
<tr>
<td>Powdered</td>
<td>15</td>
<td>-</td>
<td>-</td>
<td>10 - 20</td>
<td>Atenolol</td>
<td>88±9</td>
<td>[118]</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>23</td>
<td>Carbamazepine</td>
<td>99±1</td>
<td>[131]</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
<td>Trimethoprim</td>
<td>&gt; 80</td>
<td>[129]</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
<td>Diclofenac</td>
<td>76</td>
<td>[145]</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
<td>Ibuprofen</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

at a time t (min), C_e is the liquid phase concentration of pharmaceutical at equilibrium, V is the volume of the solution (L) and W is the mass (g) of UV-visible spectrometer.

Experimental data is always first fitted on the pseudo first order and pseudo second order equations (2 and 3) respectively.

\[ q_t = q_e (1 - e^{k_1 t}) \]  
\[ q_t = \frac{q^2 k_2 t}{1 + q e k_2 t} \]

Where \( k_1 (\text{min}^{-1}) \), \( k_2 (\text{mgg}^{-1}) \) are pseudo first and second order rate constants respectively. The adsorption equilibrium results are then described using the Langmuir and Freundlich's models as described by equations 4 and 5 respectively.

\[ q_e = K_F C_e^{1/n} \]  
\[ q_e = \frac{Q_m K_F C_e}{1 + K_F C_e} \]

Where \( K_F \) is the Freundlich adsorption constant (mgg⁻¹ (mgL⁻¹)⁻¹n); \( n \) is the degree of non-linearity, \( Q_m \) is the maximum adsorption capacity (mgg⁻¹); \( K_F \) (Lmg⁻¹) is the Langmuir affinity coefficient.

The adsorptive capacities of various adsorbents shown in Table 4 were determined basing on the isotherms discussed in this section. The details can therefore be found in the respective citations.

12. CONCLUSIONS

Literature reveals that APIs still remain a challenging class of micro pollutants both in wastewater and conventionally treated water used in day-to-day lives. Their persistence in water systems and adversity even at nano concentrations is of concern. Pyrolysis assisted chemical activation remains preferred to physical activation owing to better adsorptive properties of the AC produced by chemical activation. Unlike with other adsorbates whose adsorption is determined by characteristic numbers that cut across all adsorbents like BET surface area, pore volume, iodine number, the removal of APIs is dependent on the adsorbent bulk density, pore diameter and UVA_254 adsorption capacity. Literature also reveals that it is more effective to
augment the application of cassava peel AC in APIs removal after removal of background organic matter using the conventional water treatment systems.

Data from literature shows that granular AC performs better in adsorbing APIs than powdered AC. Cassava peels have a high potential of abating APIs from water by chemisorption owing to the presence of both positive and negative surface groups that are important in abating APIs of either charge. Physical adsorption of AC on APIs is by pore filling and mesopores are most suitable for a wide range of APIs due to the large molecules of APIs that may clog the micro and nano adsorbent pores. Cassava peel AC remains untested regarding the adsorption of APIs from wastewater. It is therefore pertinent to carry out research on the adsorption of cassava peel AC on APIs in wastewater.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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