Review

Insights into Agricultural-Waste-Based Nano-Activated Carbon Fabrication and Modifications for Wastewater Treatment Application

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Abstract: The past few years have witnessed extensive global industrial development that has led to massive pollution to most available water resources. There is no alternative to sustainable development, and the utilization of agricultural waste for wastewater treatment has been always a novel milestone in sustainable development goals. Agricultural-waste-based nano-activated carbon exhibits high porosity, great surface area, and unique surface functional groups that promote it becoming a future and sustainable solution for wastewater treatment applications. Several modification approaches have been made to further enhance the adsorption capacity and reusability of such adsorbents. In this review, we presented the potential of agricultural-waste-based nano-activated carbon as a sustainable solution for wastewater treatment. We highlighted the fabrication process and properties of different nano-activated carbons in addition to different modification approaches to enhance its adsorption capacity. Finally, we critically discussed the recent advances in nano-activated carbon applications in water treatment including its role in drinking water filtration, organic dye removal, oil spill applications, heavy metals removal and the elimination of toxic compounds from wastewater.

Keywords: agricultural waste; nano-activated carbon; adsorption; wastewater treatment; modification

1. Introduction

The world’s population has significantly increased from 3.75 billion in 1970 to over 7.91 billion last year (2021), and it is estimated to exceed 9 billion by 2050 [1]. Agricultural waste as well as agricultural pollution are predicted to increase as a result of the world’s population increasing. The last century has witnessed a huge increase in the agricultural waste production capacities of several countries including China, India, the United States of America and several parts of Africa and Europe [2,3]. However, most of this waste is biodegradable and not significantly toxic to the environment, but their accumulation and presence in large quantities can cause adverse effect to the environment. They can be utilized to solve other accumulative issues such as water contamination [4]. Various pollutants are deposited into the environment each year, such as organic compounds, heavy metals, chemicals, toxins and other hazardous materials that can nowadays be found in most of our eco-systems [5]. Ground and surface water are mostly the end-point of
many contaminants that dissolve in water and remain for years, affecting marine life as well as plants, animals and humans [6]. Several approaches have been developed for wastewater treatment, which can be categorized into physical, chemical and biological approaches [7,8]. Physical approaches are the easiest and most used ones, which include filtration, adsorption, distillation, steam and stripping, skimming and sedimentation, etc. These approaches are used to separate the liquid (water) from different organic or inorganic pollutants. Among the physical approaches, the adsorption process is the most effective and widely used approach for wastewater treatment [9].

Several natural and synthetic adsorbents can be used to attract and accumulate water pollutants onto their surfaces and eventually to precipitate it [10]. This treatment process can be a specific or generalized step; some adsorbents are able to detect specific functional groups, while others are wide-ranging. Activated carbons are the most widely used adsorbent in water treatment applications; they have been incorporated into water filters to adsorb heavy metals and other chemicals from filtrated water [11]. Nano-activated carbon is a form of activated carbon that is characterized by its high surface area, which facilitates the adsorption of pollutants into the surface. The past few years have witnessed great advances in the fabrication and modification of nano-activated carbon for different wastewater treatment applications. Several review papers have been published on biochars [12–14], its fabrication [15], properties [16] and modifications [17]. In addition, normal activated carbon has also been covered in terms of most of its aspects. Heidarinejad et al. reviewed chemical activators used to produce activated carbon [18]. Shafeeyan et al. [19] reviewed the impact of changes in the surface chemistry and formation of specific surface groups on the adsorption properties of activated carbon. Lakshmi et al. [20] focused on the different aspects of activated carbon and covered the recent trends in the development and use of various activated carbon nanoparticles as anti-microbial agents. Limited works have addressed the use of nano-activated carbon in wastewater treatment applications. The novelty of the present work is the presentation of the utilization of agricultural waste in the production of nano-activated carbon for wastewater treatment applications. In this paper we present nano-activated carbon from agricultural waste, including its fabrication and properties, and highlight different modification approaches that have been conducted to enhance its function. We also critically discuss the recent advances in nano-activated carbon applications in terms of water treatment applications including its role in drinking water filtration, organic dye removal, oil spill applications, heavy metals removal and the elimination of toxic compounds from wastewater in addition to highlighting the challenges and prospectives that face this unique material.

2. Agricultural Waste: Types, Yield and Properties

Agricultural wastes are those which are generated as a result of different agricultural operations and processes [21]. Although most of these wastes are derived from natural sources and are not toxic to the environment, they can accumulate in large quantities and subsequently cause adverse effect to humans, animals and even plants [22]. Agricultural waste can be mainly categorized into four main categories including crop residue, livestock waste, agro-industrial waste and aquacultural waste (Figure 1). Crop residue and agro-industrial waste are the largest available types of waste that are produced in large quantities on a daily and sustainable basis [23,24]. However, the lack of proper management practices of these wastes, following the lack of or limited adequate information, has continuously become a great challenge, which is too great to be downplayed.
2.1. Crop Residues Waste

Crop residues are the most common types of agricultural waste all over the world, with millions of tonnes produced every year, in which most of them are either burned or thrown into landfills. Crop residues include the straws of rice, oat, barley, and wheat, corn stoves, and the leaves of many fruit plants in addition to seed pods and shells. The global production of these wastes is projected to exceed 2802 million tonnes per year [25]. Corn stalks are the top produced crop waste with over 750 million tonnes produced per year, followed by wheat and rice with 600 and 360 million tonnes produced per year, respectively [26]. These organic wastes are rich in carbon, making them an attractive precursor material for nano-activated carbon production. Only a small portion of rice, corn, and wheat crop residues are effectively utilized in some applications such as animal fodder and/or bioenergy production, while the rest is discarded into landfill or openly burned [27]. From a chemical aspect, crop residues contain from 40 to 45% carbon, 0.6 to 1% nitrogen and 14 to 23% potassium in addition to phosphorus and microelements that are necessary for crop growth [28].

Different types of crop residues exhibit different micro-morphological properties. In general, it has been stated that most crop residues are associated with a tubular structure, thick walls, and abundant pores [29]. Thus, the resulting nano-activated carbon possesses a large specific surface area and a large pore volume and size, allowing for a great adsorption capacity. Zhang et al. [30] reported that the interior structures of rice straws have a large number of vascular bundle sheaths, intercellular canals, and medullary cavities, which give these types of waste a high porosity and large surface area. In a recent work, rice-straw-based activated carbon was prepared and chemically activated by using KOH [31]. The authors stated that their activated carbon possessed a huge surface area of 1330 m²/g, which is a lot higher than that of raw rice straw (0.77 m²/g) [32]. Comparatively, wheat straw exhibits linear and multi-cavity structures that mostly bridge between the micro and nano pores that give this waste its complex network structure [33]. The properties of nano-activated carbon-based crop residues are basically dependent on the types of residues, and a good understanding of the characteristics and properties of each raw material is essential to fabricate nano-activated carbon with the desired properties.
2.2. Livestock Waste

Livestock waste consists of wastewater, solid manure from different farm animals and liquid manure. Out of these types of waste, solid manure has been used for the preparation of activated carbon as an environmentally friendly solution. Topcu et al. [34] successfully utilized poultry manure as a precursor material for activated carbon production. The production of animal manure in the European agricultural sector alone has exceeded 1500 million tonnes per year, which opens another source for activated carbon production [35]. Animal manure is a renewable resource as it basically comes from cellulogenic feed and undigested residue, which is excreted by livestock animal species. Traditionally, animal manure is used as a fertilizer without any proper treatment, which can cause significant environmental problems including greenhouse gas emissions, public hazards (asphyxia poisoning and infectious pathogens), air quality deterioration and water pollution [36]. As a sustainable and eco-friendly solution, Tsai et al. [37] successfully utilized cow manure as a precursor material for activated carbon production and reported its great properties and a surface area of more than 950 m$^2$/g. Owing to its organic source and its high carbon content, animal manure can be thermally converted (or further modified) into various forms of carbon materials and energy sources [38]. However, the low energy yield and air pollution resulting from manure processing for energy production has added additional value to it as a suitable and sustainable adsorbent for several environmental applications.

2.3. Agro-Industrial Waste

Agro-industrial waste is another type of agricultural waste that generated as a by-product from several food- and beverage-processing industries. Huge amounts of these wastes are produced every year. Sugarcane bagasse, for example, is generated from the sugar manufacturing industries, and approximately 180.73 million metric tons of it is produced every year, and it is estimated to reach 221 million metric tons in 2024 [39]. Other industries such as palm oil are also generating over 35.19 million tonnes of waste out of 85.84 million tonnes of the fresh fruit of the palm plant [40]. The huge amount of agro-industrial waste makes them highly attractive sources of activated carbon, and a significant number of studies have been conducted on the utilization of such waste in nano-activated carbon preparation [41,42].

2.4. Aquaculture Waste

The aquaculture industry is considered to be one of the fastest growing food production industries due to the fast-growing nature of fish as well as aquatic plants. Akinwole et al. [43] stated that feed has become the primary source of waste in aquaculture, followed by fish faeces. Both are harmful to fish and need to be removed as soon as possible, which means they can be utilized in nano-activated carbon fabrication [44]. In fish culture systems, the amount of released and uneaten feed varies with the system type. However, daily treatment is highly required in such systems, which generate an accumulative amount of such waste. Therefore, a general management plan and smart utilization is highly needed [45]. Limited works have been conducted on the management of aquacultural waste, and activated carbon is mostly used to treat water polluted by toxic materials in culture systems [44,46,47].

3. Agricultural-Waste-Based Nano-Activated Carbon: Fabrication and Properties

Generally, nano-activated carbon can be fabricated from different precursors including agricultural and forestry residues. These precursors are rich in carbon, leading to the production of high-yield activated carbon [48]. The production of nano-activated carbon can be achieved by grinding the clean waste into fine particles and then conducting thermal treatment of these particles (pyrolysis) followed by physical and/or chemical activation. Figure 2 presents illustration of the fabrication process starting from agricultural waste.
Pyrolysis is an essential process in the fabrication process, which determines most of the nano-activated carbon’s properties. Om Prakash et al. [49] recently synthesized nano-activated carbon using arhar fiber biomass and a novel technique consisting of two-stage pyrolysis followed by chemical activation. In this study, the authors used different temperatures ranging from 700 to 900 °C and reported that the one prepared at 800 °C exhibited the highest surface area (504.6 m²/g) with tiny surface micropores of a 20 Å diameter. Although a higher temperature was used, the optimum properties were not associated with the highest temperature. However, different precursor materials have different optimum temperatures for the best adsorption capacity. The optimal temperature and time depend on the type of precursor material and activation approach. It has been reported that carbon dioxide activation requires 800 °C and 1 h of holding time, compared with steam activation that requires only 700 °C and the same amount of time [50].

Physical activation can be achieved by further thermal treatment, steam exposure and microwave and/or ultrasound treatment [51]. The advantages of physical activation methods are their simplicity, the fact that they do not involve any chemical usage and the resulting production of microporous structures rather than the microporous structures achieved in the chemical activation process [52]. Carbon dioxide activation was found to produce a higher surface area and micropore volume than steam activation. In a recent study, the maximum surface area of CO₂-activated carbon was 789 m²/g compared to steam-activated carbon with a maximum surface area of 552 m²/g [50]. Owing to the decomposition of cellulosic material in plant waste, the yield of nano-activated carbon decreases with increasing the temperature [50]. Thus, reheating activated carbon could further reduce the production yield. Chemical activation is more common, using several chemical compounds such as KOH, ZnCl₂, K₂CO₃ and CaCl₂. In the work of Gan, the author discussed different chemical activation agents and their effects on the adsorption performance [53]. Although chemical activation may involve the excessive use of chemical agents, several studies have reported an adsorption capacity of up to 99% of water pollutants from water [54]. Conceptually, chemical agents with dehydration and oxidation properties are

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**Figure 2.** Schematic illustration of agricultural-waste-based nano-activated carbon fabrication.
more suitable for the activation of different plant-based carbons [55]. Refer to Table 1 for a summary of the different studies that have used different activation approaches.

Table 1. Comparison of the functional properties of using different activation approaches for activated carbon preparation.

<table>
<thead>
<tr>
<th>Type of Activation</th>
<th>Precursor Material</th>
<th>Pyrolysis Conditions</th>
<th>Activation Agent</th>
<th>Removing Material</th>
<th>Adsorption Capacity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical activation</td>
<td>Palm kernel shells</td>
<td>700 W for 30 min</td>
<td>Steam</td>
<td>Herbicides</td>
<td>11 mg/g</td>
<td>[56]</td>
</tr>
<tr>
<td></td>
<td>Cattle manure</td>
<td>600 °C for 60 min</td>
<td>Microwave and ultrasound CO₂</td>
<td>Elemental mercury</td>
<td>7.43 mg/g</td>
<td>[57]</td>
</tr>
<tr>
<td></td>
<td>Corn cob residue</td>
<td>600 W for 20 min</td>
<td>Microwave and H₃PO₄</td>
<td>Hydrogen sulfide</td>
<td>868.45 mg/g</td>
<td>[58]</td>
</tr>
<tr>
<td></td>
<td>Bamboo</td>
<td>900 °C for 120 min</td>
<td>Steam and thermal</td>
<td>Organic dyes</td>
<td>183 mg/g</td>
<td>[59]</td>
</tr>
<tr>
<td></td>
<td>Prawn shells</td>
<td>800 °C for 180 min</td>
<td>KOH and HCl</td>
<td>Heavy metals</td>
<td>560 mg/g</td>
<td>[60]</td>
</tr>
<tr>
<td>Chemical activation</td>
<td>Pistachio shells</td>
<td>1000 °C for 240 min</td>
<td>CaHPO₄</td>
<td>Organic dyes</td>
<td>-</td>
<td>[48]</td>
</tr>
<tr>
<td></td>
<td>Lignocellulosic waste</td>
<td>600 °C for 120 min</td>
<td>H₃PO₄</td>
<td>Pesticide</td>
<td>35.7 mg/g</td>
<td>[62]</td>
</tr>
<tr>
<td></td>
<td>Cashew nut shells</td>
<td>500 °C for 120 min</td>
<td>ZnCl₂</td>
<td>Dyes</td>
<td>476 mg/g</td>
<td>[63]</td>
</tr>
<tr>
<td></td>
<td>Animal bone waste</td>
<td>600 °C for 120 min</td>
<td>Orthophosphoric acid</td>
<td>Heavy metals</td>
<td>27.86 mg/g</td>
<td>[64]</td>
</tr>
<tr>
<td></td>
<td>Molasses</td>
<td>500 °C for 120 min</td>
<td>H₃PO₄</td>
<td>Organic dyes</td>
<td>625 mg/g</td>
<td>[65]</td>
</tr>
</tbody>
</table>

4. Modifications of Agricultural-Waste-Based Nano-Activated Carbon

Although most nano-activated carbons exhibit a sufficient adsorption capacity for wastewater pollutants, scientists have always convinced themselves that much more can be done to enhance the adsorption performance of nano-activated carbon. Several approaches have been investigated including incorporating nano-activated carbon with metal oxides, enhancing the porosity and surface area of the particles using chemical or physical agents and the incorporation of activated carbon with specific chemical compounds for specific adsorptions.

4.1. Incorporation of Nano-Activated Carbon with Metal Oxides

To enhance the affinity of nano-activated carbon to the adsorption of heavy metals and other inorganic compounds, several elemental iron and iron (hydr)oxides have been used, especially for arsenic removal [66]. Nano-sized zero-valent iron was incorporated with activated carbon in one study, using ferrous sulfate impregnation followed by chemical reduction by NaBH₄ [67]. The authors reported the significant enhancement of arsenite and arsenate absorption at pH 6.5, and they stated that the removal markedly decreased by using phosphate and silicate. However, metal cations such as Ca²⁺ and Mg²⁺ are known for their adsorption enhancement, while ferrous iron (Fe²⁺) suppresses adsorption. In another recent investigation, nano-sized hematite-modified nano-activated carbon was prepared by coating the activated carbon particles with α-Fe₂O₃ nanoparticles [68]. Such modification enhanced the adsorption of nano-activated carbon by three times more than non-modified one, the removal process occurred in shorter duration and the authors were able to effectively regenerate their activated carbon by using HCl with a minor reduction in the adsorption efficacy after four desorption–adsorption cycles.

The use of iron-based nano particles also has the advantage of easy regeneration using a magnetic field compared with other metallic oxides. Khalil et al. [69] developed this approach by using an ethanol medium and acid thermal treatment to produce modified nano-scale zero-valent/activated carbon to enhance the removal of nitrate and phosphate from water. The authors reported that the thermal treatment of nano-activated carbon before the supporting nano-scale zero-valent modified the texture and surface of the activated carbon, leading to an enhancement of the surface chemistry properties and thus a better attraction of contaminant anions (Figure 3). The same authors reported that their optimum modification enhanced the removal efficiency of nitrate by more than 170%, while the complete removal of phosphate was achieved, which came about due to the modified surface structure of the activated carbon. Such modification can be also applied with other types of activated carbon for the removal of other pollutants. Metal oxide particles supported on activated carbon can significantly enhance the adsorption and desorption efficacy of the materials and provide effective wastewater treatment.
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Figure 3. Schematic illustration of textile and surface chemistry modification of nano-scale zero-valent/activated carbon for the removal of nitrate and phosphate from water. The graphs show the removal efficiency of both nitrate and phosphate alone and combining together. Reprinted with permission from Ref. [69], 2017, Elsevier.

4.2. Incorporation with a Specific Chemical Compound

Several chemical compounds have been incorporated with nano-activated carbon to target the adsorption of specific heavy metals or other toxic materials from aqueous solutions. In one recent study conducted by Sabermahani & Noraldiny [70], they developed a facile and low-cost activated carbon from apricot fruit nuclei and activated it with H$_3$PO$_4$ for the removal of thallium (I). The authors modified their activated carbon by incorporated it with rhodamine B for the specific adsorption of thallium (I). The addition of rhodamine B significantly enhanced the adsorption efficiency of the activated carbon. Owing to the strong attachment between the dye and activated carbon particles, the modified particles exhibited better adsorption characteristics compared to the non-modified ones. In a different investigation, Deng et al. [71] used pristine feedstock to fabricate activated carbon and then used chitosan and pyromellitic dianhydride as chemical modifiers. The authors stated that their modified activated carbon exhibited an increased number of surface functional groups compared with the non-modified one, which led to a better adsorption of heavy metal ions. The addition of chitosan and pyromellitic dianhydride supplied the particles with nitrogen-rich functional groups in addition to the C=C and N–C=O, which were mainly responsible for the adsorption of Pb, Cd and Cu from water. Zhou et al. [72] used the same modification principal and reported a significant enhancement in the adsorption capacity in a markedly shorter time.
Several functional groups such as oxygenated groups and phosphate can be incorporated on nano particle surfaces to promote metal particle anchorage, which facilitates and speeds up the adsorption of heavy metals and other metallic-based toxic compounds. Several studies have used graphene oxide as a chemical modifier to enhance the adsorption capacity of activated carbon, which is also a carbon-rich agent [73,74]. Such modification was conducted prior to the pyrolysis process, which resulted in oxygen-rich surface-functional groups. Owing to the unique structure of graphene and its ability to integrate within the mixture after the pyrolysis, the prepared activated carbon possessed a high surface area with a significantly enhanced adsorption capacity [73,74]. The surface modification of Pongamia-pinnata-shells-based acid-activated carbon has been conducted in different work using a cationic surfactant (Cetyltrimethylammonium bromide) for the specific adsorption of organic dyes [75]. The authors stated that such modification significantly enhanced the uptake capacity of the activated carbon for organic dyes, which could be used as a cleaner alternative for dye adsorption from aqueous solutions. The same authors were able to regenerate their modified activated carbon and reuse it several times without any significant loss in adsorption capacity.

4.3. Enhanced Porosity and Surface Area

As an adsorption material, a large surface area is an essential character for most wastewater treatment applications. Reducing the particle size and porosity can significantly increase the surface area, leading to an enhanced adsorption efficiency. Lignocellulosic activated carbon was prepared and modified by impregnation with the precursor material in a Cu(NO$_3$)$_2$ solution [76]. The authors reported a higher mesoporosity in the modified particles compared with the non-modified ones, which enhanced their adsorption capacity. In different study, Huang et al. [77] investigated the effect of different activation parameters in the porosity and morphological characteristics of wood-sawdust-based activated carbon fibers. An enhanced porosity and a greater surface area were achieved with KOH activation and a temperature of above 800 °C, which generated nano pores ranging from 0.8 to 1.1 nm. Enlarged pores can be obtained with increasing the KOH/material ratio and prolonging the activation time, and the authors were able to obtain larger pores from 2 to 5 nm [77]. The adsorption capacity of the adsorbent is directly proportional to increasing the surface area, which is also directly proportional to the porosity. Depending on the waste that needs to be absorbed, the pore size and surface functional groups of nano-activated carbon can be easily adjusted, especially with chemical activation. For this purpose, Abuzalat et al. [78] fabricated and modified nano-activated carbon from green algae Ulava lactuca using a novel and facile approach. The authors used zinc chloride for the activation and modification of their nano-activated carbon and reported meso–micro porous structures with a significantly higher surface area (1486.3 m$^2$/g). With such a surface area, the authors investigated the adsorption capacity of the porous nano-activated carbon in the adsorption of organic dyes and stated a maximum adsorption capacity of 149.26 mg/g, which indicated the high ability of such a modified activated carbon in the adsorption of organic dyes. In a different investigation, Jain et al. [79] enhanced the porosity of sunflower-head-waste-based nano-activated carbon and evaluated it for the removal of Cu(II), Cr(VI) and Cd(II) ions from polluted water. The authors used mineral acids as the activation agents to increase the porosity of their nano-activated carbon, and they stated that sulphuric acid activation produced the highest surface area pore width and volume in addition to the highest porosity (Figure 4). Having such great characteristics, the nano particles immediately adsorbed 89.4% and removed 74.5% of the Cr(VI) and Cd(II) in the first 2 min.
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![Figure 4](https://example.com/figure4)

**Figure 4.** Illustration of sunflower-head-waste-based nano-activated carbon; (a) scanning electron microscope images at different magnifications, (b) effect of temperature on the adsorption, and (c) schematic drawing of adsorption process of heavy metals. Reprinted with permission from Ref. [79], 2018, Elsevier.

### 4.4. Other Modification Techniques

The facile and eco-friendly modification of agricultural-waste-based nano-activated carbon has always been a great challenge due to the need for physical and/or chemical agents to enhance the properties of the adsorbent materials [11]. However, although some modification may not be completely eco-friendly, the enhanced removal of toxins and undesired material from wastewater is worth this slight sacrifice. A bimetallic platin-ruthenium nano adsorbent was used to modify and support nano-activated carbon using a thermal decomposition process [80]. The authors used the modified activated carbon for methylene blue dye removal from aqueous solutions and reported a great enhancement in the adsorption capacity, reaching 569.4 mg/g under the optimum conditions. In a different study, Deng et al. [81] modified their activated carbon by loading silver nano particles in its pores in order to enhance bacterial activation in drinking water. The authors used Escherichia coli as a standard bacterium for their investigation and reported that surface-bound silver (Ag I) was slightly converted to Ag as a result of structural reducing groups on the surface of the activated carbon (Figure 5). The attached silver nanoparticles were able to directly sterilize most of E. coli in the treated water by catalyzing O₂ and H₂O in the solution and generating reactive oxygen species (ROS). ROS possess great disinfection properties for most microorganisms by the oxidation sterilization process [82]. The same authors
stated that the pH strongly affected the inactivation process, and a neutral pH was the optimum compared with acidic and basic pH values. Figure 6 presents illustration of silver-nano-particles-based modified activated carbon for water disinfection and sterilization applications. Such modifications can open the door to reducing the excessive use of chlorine. Modified activated carbon may work in reducing toxic materials and disinfecting water from microorganisms at the same time without the need to further add water disinfectants. Other modification techniques have been used to modify nano-activated carbon, including ball milling and hydrothermal synthesis to further reduce the size of the particles [83,84], co-precipitation to integrate functional groups within the pores of the activated carbon [85], succinylation [86], and solvothermal treatment [87,88].

Figure 5. Modified activated carbon for water disinfection; (a) schematic illustration of the fabrication process, (b) SEM images showing the pore size and silver nanoparticles attachments and (c) the sterilization mechanism of modified activated carbon. Reprinted with permission from Ref [81], 2022, Elsevier.

5. Agricultural-Waste-Based Nano-Activated Carbon for Wastewater Treatment Applications

Massive industrial development has accelerated the accumulation of waste in the environment, which eventually ends up in water bodies. Different agricultural wastes have been extensively investigated as precursor materials to solve the issue of water pollution [89]. They are suitable raw materials for the fabrication of enhanced nano-activated carbon, which can be used for drinking water filtration, the removal of dyes and organic compounds, the removal of heavy metals and the elimination of toxins and chemical compounds in addition to solving oil spill issues and in other wastewater treatment applications.

5.1. Drinking Water Filtration

Water filtration is an essential process that removes or reduces the concentration of most of the pollutants including suspended particles and microorganisms as well as undesirable chemical compounds from contaminated water. Several approaches containing filters and membranes have been fabricated for this purpose including micro-filtration, nano-filtration, reverse osmosis, pervaporation and ultrafiltration membranes [90]. Nano-
activated carbons have gained tremendous attention recently in drinking water filtration applications due to their high surface area, nano porosity and high adsorption and removal performance in terms of organic as well as inorganic pollutants present in drinking water and wastewaters [91,92]. In a recent investigation, granular coconut-shell-based activated carbon was prepared and evaluated for the adsorption and removal of polystyrene nano plastics from drinking water [93]. Owing to the negatively charged granular coconut-shell-based activated carbon that interacted with the positively charged nano plastics, the authors were able to achieve a maximum adsorption capacity of more than 2.20 mg/g. The presence of dissolved organic matter significantly enhanced the adsorption capacity of the activated carbon, due to changing the surface charges on the nano plastics and the presence of divalent ions (Figure 6a). In a similar work, Altmann et al. [94] investigated a pilot scale of granular activated carbon integration into coagulation/filtration. The authors combined the adsorption of that activated carbon with deep-bed filtration (Figure 6b), and they were able to effectively remove both suspended solids and phosphorus from drinking water.

![Figure 6](image-url)

**Figure 6.** Granular activated carbon-based drinking water filters: (a) the adsorption and removal of polystyrene nano plastics, and (b) the removal of suspended solids and phosphorus from drinking water. Adapted with permission from ref. [93], 2021, Elsevier (a), and [94], 2016, Elsevier (b).

### 5.2. Removal of Dyes and Organic Compounds

Dyes are widely used in several industries such as the textile industry, paper, plastics, cosmetics, etc. Synthetic dyes are a specialized class of organic pollutants that, in most cases, are directly discharged into environmental ecosystems as wastewater from their industries [95,96]. These organic pollutants exhibit complicated structures from their aromatic assembly, making them difficult to degrade in natural conditions. Thus, it is necessary to develop an eco-friendly and cost-effective approach to treat water polluted with such pollutants. In a recent study, nano-activated carbon was prepared from Maghara raw Egyptian coal and investigated for the removal of methylene blue dye from wastewater [97]. In this study, the activated carbon particles had an average diameter of 38 nm and pore volume of over 0.183 cm³/g, resulting in a high adsorption capacity of 28.09 mg/g. In different
study, Mousavi et al. [98] used corn stalks to prepare nano-activated carbon for the removal of rhodamine B dye from contaminated solutions. The authors were able to achieve a 5.6 mg/g adsorption capacity at the optimum conditions, which fitted pseudo-second-order kinetics and the Freundlich isotherm model. Owing to the porous surface and high surface area of nano-activated carbon, organic dyes can be easily adsorbed into these particles, resulting in great removal efficiency. In term of dye adsorption using of nano-activated carbon, the regeneration of the adsorbent has been always a great challenge due to activated carbon/dye bonding. Feiqiang et al. [99] developed magnetic activated carbon using a one-step approach for toxic dye removal from polluted water. The authors fabricated the adsorbent under a CO\(_2\) atmosphere and reported that the CO\(_2\) enhanced the surface area of the activated carbon, which enhanced the adsorption of the dyes. The authors were able to easily remove the dyes using an external magnetic field. In the same manner, Liu et al. [100] used the same principal for the fast and effective removal of organic dyes from an aqueous solution. The surface area and functional groups played a fundamental role in the dye and toxic material adsorption mechanism by attracting bonding between the chemical groups (Figure 7). The authors were able to achieve a great adsorption capacity of 182.48 mg/g and 150.35 mg/g for rhodamine B and methyl orange, respectively. Owing to the incorporation of iron oxide, the authors were able to easily regenerate and separate their adsorbent. Such effects and highly efficient adsorbents with a rapid magnetic separation have promising applications in different wastewater treatments.

![Figure 7. Schematic drawing of using magnetic activated carbon in dye removal; (a) the application of Fe\(_3\)O\(_4\)/AC sample for removing rhodamine B and methyl orange from the aqueous solution, and (b) the adsorption mechanism. Reprinted with permission from Ref. [100], 2019, Elsevier.](image-url)
5.3. Removal of Heavy Metals

Heavy metals pollution has become a major concern in recent times due to massive industrial development. Some heavy metals function as micro or even macro nutrients for certain animals and plants. However, in high concentrations they are highly toxic to most living organisms [101]. Hexavalent chromium is a toxic form of the heavy metal chromium that can irritate the nose, lungs and throat and cause other adverse health effects. Li et al. [68] developed modified activated carbon that was able to significantly remove most of the hexavalent chromium from water. The authors coated their activated carbon with iron oxide nanoparticles using a facile impregnation approach, and they reported that this enhanced the adsorption capacity by three times more than the non-modified activated carbon.

Steam activation has been used to enhance the activity of carbon adsorbents in heavy metal removal applications. Lou et al. prepared activated carbon from pine sawdust using steam activation and reported an enhanced adsorption capacity [102,103]. Although the surface area was slightly reduced, the steam activation seemed to enhance the adsorption of the heavy metals. In different study, Valentín-Reyes et al. [104] investigated chemically activated carbon with a high surface area for the removal of hexavalent chromium (Cr(VI)) from water. Changing the surface chemistry during the activation process was proposed by the authors as the reason for enhancing the adsorption mechanism. A significant number of studies have been conducted on evaluating the adsorption capacity of different agricultural-waste-based nano-activated carbon on the adsorption of heavy metals (Table 2).

Table 2. Illustration of studies presenting the adsorption capacity of different agricultural-waste-based nano-activated carbon.

<table>
<thead>
<tr>
<th>Agricultural Waste</th>
<th>Pyrolysis Condition</th>
<th>Type of Metal</th>
<th>Surface Area (m²/g)</th>
<th>Maximum Adsorption (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut shell</td>
<td>Commercial</td>
<td>1~</td>
<td>1220</td>
<td>41.2</td>
<td>[105]</td>
</tr>
<tr>
<td>Bamboo waste</td>
<td>700 °C for 2 h</td>
<td>Cd(II)</td>
<td>6.79</td>
<td>73.45</td>
<td>[106]</td>
</tr>
<tr>
<td>Pig manure</td>
<td>700 °C for 2 h</td>
<td>Cd(II)</td>
<td>11.37</td>
<td>77.34</td>
<td>[106]</td>
</tr>
<tr>
<td>Kenaf core fiber</td>
<td>400 °C for 1 h</td>
<td>As (III)</td>
<td>1031</td>
<td>422.9</td>
<td>[107]</td>
</tr>
<tr>
<td>Rape straw</td>
<td>300 °C for 2 h</td>
<td>Pb(II)</td>
<td>699.9</td>
<td>253.2</td>
<td>[108]</td>
</tr>
<tr>
<td>Hazel nut shell</td>
<td>700 °C for 2 h</td>
<td>Hg</td>
<td>-</td>
<td>80.0</td>
<td>[109]</td>
</tr>
<tr>
<td>Gingko leaf</td>
<td>400 °C for 1.5 h</td>
<td>Cu(II)</td>
<td>310.00</td>
<td>59.90</td>
<td>[110]</td>
</tr>
<tr>
<td>Lignite and poplar leaves</td>
<td>600 °C for 0.5 h</td>
<td>Pb(II)</td>
<td>805.86</td>
<td>10.55</td>
<td>[111]</td>
</tr>
<tr>
<td>Pine tree residue</td>
<td>600 °C for 4 h</td>
<td>Cd(II)</td>
<td>N.A</td>
<td>85.8</td>
<td>[112]</td>
</tr>
</tbody>
</table>

5.4. Oil Spill Separation

Large oil spills are a major environmental problem that occurs as a result of accidents caused by either human error or natural calamities. These oil spills have a significantly toxic and harmful impact on different environmental eco-systems, which eventually will affect human health [113]. In recent years, activated carbon has been investigated to solve oil spill issues. Shokry et al. [114] developed nano-magnetic activated carbon from waste biomass (hyacinth roots) for facile oil spill separation by using an external magnetic field. The authors reported that the original biomass exhibited only a 2.2 g oil /g oil spill adsorption affinity compared with their modified nano-magnetic activated carbon that showed a 30.2 g oil/g adsorption affinity after one hour of placing 1 g of their activated carbon in one litter. The authors were also able to easily separate the magnetic nano-activated carbon from treatment media by using an external magnetic field.

Although great advances have been made, the commercialization of cost-effective, reusable and eco-friendly sorbents for oil separation is yet to be achieved on a large-scale level [115]. Hammouda et al. [116] developed an efficient and eco-friendly magnetic activated carbon from plant biomass for oil spill applications. The authors coated magnetic nanoparticles with activated carbon and then made a soybean oil and stearic acid surface decoration. This modification made the magnetic fabricated composite possess an excellent amphiphilicity and a great adsorption capacity to a range of oils. In a different study, coconut-shell-based nano-activated carbon was incorporated with iron oxide nanoparticles and investigated in an oil spill treatment experiment [117]. The authors reported an
excellent and fast oil retention capacity, with facile recovery by using an external magnetic field. The cost effectiveness of agricultural-waste-based nano-activated carbon and their whole fabrication and treatment processes in the required bulk quantities suggest great advances for these adsorbents in oil removal applications.

5.5. Removal of Toxins and Pharmaceutical Compounds

Several environmental toxins are highly abundant in eco-systems as a result of natural and/or anthropogenic processes [118]. Polycyclic aromatic hydrocarbons are one of these toxins that are released from the burning of coal, vehicle emissions and the burning of biofuels and biomass [119]. These toxins exhibit a highly hydrophobic nature, making them difficult to biodegrade, and thus they enter the food chain through either polluted air, sand and/or water [120]. To solve this issue, Inbaraj et al. [121] developed nano-activated carbon from green tea leaf waste. The authors evaluated their nano-activated carbon for the adsorption of four priority polycyclic aromatic hydrocarbons, and they reported that, owing to the unique spherically shaped and cubic spinel structure of the nano particles, the surface area was found to be 118.8 m²/g. The adsorption capacity of these nano particles for the four priority polycyclic aromatic hydrocarbons ranged from 19.14 to 28.08 mg/g. The same authors also applied their nano-activated carbon to mineral water, tap and river water, resulting in up to an 89% removal of these toxins from mineral water and complete removal from tap and river water. In a different study, different agricultural wastes were used to prepare activated carbon fibers for the removal of cyanobacteria toxins (microcystins) from drinking water [122]. The authors were able to remove more than 98% of the toxin after only 10 min of contact time by using sugar-cane-bagasse- and pine-wood-based activated carbon fibers. Nano-activated carbon has also been used to eliminate toxic herbicides as a cost-effective, easy and effective technique. Rambabu et al. [123] developed nano-activated carbon from date-palm coir (DPC) waste via an easy and single-step carbonization and chemical activation process for the elimination of a highly toxic 2,4-dichlorophenoxyacetic acid herbicide. The nano-activated carbon exhibited a graphitic structure and a flaky morphology, with a particle size and surface area of 163 nm and 947 m²/g, respectively (Figure 8). The authors were able to remove more than 98.6% of the herbicide from the contaminated water with a small dosage of nano-activated carbon. The same authors evaluated the economic value of their nano-activated carbon and stated that the economic value of the nano-activated carbon was $3/kg, and it could be reused without any significant loss in the adsorption capacity. Such an economic analysis supports our hypothesis that agricultural-waste-based nano-activated carbon can be the future of wastewater treatment applications.

![Figure 8. Schematic illustration of nano-activated carbon prepared from date-palm coir waste and its usage in toxic herbicide removal. Reprinted with permission from Ref. [123], 2021, Elsevier.](image-url)
6. Conclusions and Perspectives

Different agricultural wastes can lead to serious environmental and health problems depending on their type and source. The proper management and utilization of agricultural waste can have positive impacts on the environment in terms of reducing both the waste and removing pollution from water bodies. The fabrication of nano-activated carbon from such sustainable resources has several advantages apart from their potential adverse impacts. Agricultural wastes are extremely low cost and eco-friendly, which can reduce the overall cost of the production process of wastewater treatment systems. This is meaningful, as the price of these systems and of activated carbon in particular have both increased over time. Among the two activation approaches of activated carbon, physical activation is more time consuming than chemical activation, which could slightly increase the cost in addition to the difficulties in controlling the pore size and porosity of the nano-activated carbon particles. Thus, chemical activation and modification has become more prevalent. Activated carbon, due to its current cost of manufacturing, will remain the most prominent carbon-based water filtration material for the time being, with chemical modifications being used to improve the capture capacity and efficiency, thereby maintaining its relevance. As the cost of fabricating carbon nanotubes and graphene are reduced, it is highly likely that these carbon nanomaterials will be developed into advanced filtration devices or as additional components to a broad spectrum of nano-activated carbon devices used to capture specific contaminants. Ighalo et al. [124] stated that the cost of the adsorbent material used could vary depending on the method of activation employed, with chemical activation being more expensive than physical activation. Other factors can also affect the cost, including industrial-grade precursors, the chemicals used in any stage of preparation, adsorption capacity, selectivity, operational cost and the adsorbent degradation rate [125–127]. These factors should be taken into consideration before any attempt at large-scale production of the adsorption materials. The modification of nano-activated carbon allows these advanced adsorbents to specifically target the desired pollutants even in tiny amounts, which is highly beneficial in drinking water treatment applications. The future of water treatment will witness the high utilization of nano-activated carbon-based filters and treatment systems to eliminate toxic and undesired compounds. The activation, modification and application of nano-activated carbon are increasingly being developing every day, and the near future will witness the development of high-performance nano-activated carbon that is able to generally adsorb most wastewater pollutants with a reasonable cost of production.


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