Comparison of Modified Peels: Natural Peels or Peels-Based Activated Carbons for the Removal of Several Pollutants Found in Wastewaters

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Abstract: Wastewater treatment has attracted much attention in recent years as a potential source of water, and there are some concerns about its safety for human use. Eco-friendly and cost-effective adsorbent materials were successfully synthesized from several peels, such as orange, banana, pomegranate, avocado, kiwi, etc., and were used as natural adsorbents or as activated carbons derived from these peels for water and wastewater treatment. In this review, the latest research focusing on the effective modification of these peels for the removal of several pollutants found in wastewaters are summarized and compared, such as pharmaceuticals, dyes, heavy metals, and anions that are released in waste and have a negative impact on human and animal health. In this review, focus is given to activated carbon produced from fruit peels. Moreover, fruit peels as adsorbent materials, without previously being converted to activated carbon, are of limited use in the recent literature.

Keywords: pharmaceuticals; dyes; chromium; arsenic; fluoride; adsorption; modification

1. Introduction

Several substances in untreated or inadequately treated wastewater are known to be toxic to humans, animals, and plants, and consequently have adverse effects on the environment [1]. Industry is the main source of water pollution, as these industries comprise the tannery, distillery, pulp and paper, textile and dye, food, and metallurgical industries, among others [2,3]. Therefore, if these wastes are released into aquatic ecosystems without tolerable treatment, they lead to water pollution. Water pollutants can be categorized [1] as organic pollutants, such as, among others, pharmaceuticals and dyes, and inorganic pollutants such as heavy metals and ions, e.g., fluoride. Therefore, this review focuses on these types of pollutants.

Particularly, extensive drug use and insufficient management practices have increased these pollutants’ presence in wastewater and, consequently, in surface and ground water. These pharmaceutical compounds, despite their beneficial effects at precise concentrations in the body, cause contrary effects when they are found in water [4,5]. Thus, it is important to apply appropriate techniques both for the correct determination of pharmaceutical groups and for their removal. Moreover, the category of organic pollutants also includes the dyes released in wastewater mainly from the textile industries, and consist of very hazardous compounds that have the potential to be toxic and to cause cancer in humans [6]. Regarding inorganic pollutants, heavy metal ions and metalloids have several harmful effects on humans and degrade water quality [7]. Among them are chromium (Cr), cadmium (Cd), mercury (Hg), arsenic (As), lead (Pb), and many others, which can be found in several
places around the world in amounts above the permissible limits for drinking water [8]. In addition, fluoride is a common pollutant found in a variety of industrial wastewaters [9]. Although fluoride is beneficial to human health at concentrations in the range of 0.7–1.2 mg/L, providing protection against dental caries, at concentrations above the WHO limit (1.5 mg/L), it has been stated that it causes skeletal and dental fluorosis [9,10].

Adsorption is considered as one of the widely used methods for the removal of organic and inorganic pollutants from drinking water and industrial wastewater [11]. Currently, there is a plethora of commercially available adsorbents applied in various treatments, such as zeolites [12,13], graphene oxide [14–16], chitosan [17], and activated carbon [18,19], or combinations thereof [5]. Activated carbon is highly effective in removing organic and inorganic pollutants, and its porous structure and surface functional groups are crucial [20]. However, the economic practicability of activated carbon may be a drawback, despite its widespread use. Thus, researchers have studied other sources of adsorbents, such as agricultural wastes, used as natural adsorbents [21], that offer an economical and sustainable solution for several pollutants found in wastewater [22]. Examples of these agricultural wastes are some shells [23], roots [24], fruit peels [25–27], etc. Particularly, banana peels in powder form were examined as adsorbents for removing MB dye and pesticides, such as glyphosate and atrazine [28], or chlorpyrifos by lemon peels [29], from water. In addition, other kinds of peels, such as orange, pomegranate, kiwi, etc., have been found to be effective for removing several dyes from wastewaters [30,31] and pharmaceuticals [32]. In recent literature, Artocarpus genus fruit peels were also examined as raw peels or as biomass for activated carbon production for the removal of various pollutants present in aqueous streams [33].

Therefore, this review focuses on summarizing and comparing recent trends in sustainable and cost-effective adsorbents using low-cost agricultural wastes, such as modified peels or activated carbons derived from them, when used as natural adsorbents for the removal of several pollutants found in wastewater.

2. Biomass-Based Activated Carbons

Activated carbon (AC) adsorption has been shown to be an appropriate method for removing pollutants from wastewater because of its adaptability, effectiveness, vast surface area, easy operating method, and economic feasibility [34]. AC’s large specific surface area and well-formed pore structures facilitate physical adsorption, and the many oxygen-containing functional groups on the surface of AC supply Brønsted and Lewis acidic centers. However, developing inexpensive and effective ACs remains a problem. As a result, recyclable materials such as agro-industrial waste are regarded as the best manufacturing antecedents [35]. These waste products have greater carbon percentages and lower percentages of ash [36]. Many studies have investigated the development of low-cost adsorbents from agricultural wastes in order to eliminate heavy metals, fluoride ions, pharmaceutical residues, and dyes. Various types of peels, including banana, pomegranate, orange, cassava, shaddock, potato, etc., have been employed as natural sources for the production of activated carbon [37–40]. They are a low-cost option for bio-materials that are, additionally, ecologically friendly.

Physical or chemical activation, or both, represent a common method for preparing AC. Physical or chemical activation, or both, constitute a common method for preparing AC. Physical activation involves the carbonization and activation of precursor substances at high temperatures, utilizing gases such as nitrogen, argon, xenon, CO₂, or steam [41]. Chemical activation is less complicated and produces better results than physical activation; therefore, it is a preferable option in the case of agricultural waste [37]. The most frequent activation agents are ZnCl₂, H₃PO₄, and KOH/NaOH; nevertheless, these activating agents are poisonous and very corrosive. K₂CO₃, which is less hazardous, is a better option [42]. However, chemical activation requires a high amount of oxidizing agents, increasing the cost, while physical activation is a greener approach [43]. The fabrication of AC requires a lengthy duration of time and an elevated carbonization temperature, which makes
the procedure expensive on a commercial basis. As a result, the cheaper manufacturing and effective utilization of AC for many purposes remain important challenges [44]. For economically viable AC generation, minimal activation time and temperature are required.

2.1. Dye Removal

Dye wastewater has grown into a critical issue that stifles quick economic growth, harms the health of individuals, and negatively impacts the natural world. The majority of dyes are poisonous organic chemicals with high chemical stability; they are difficult to break down and have carcinogenic, teratogenic, and mutagenic properties [45]. These hazardous substances, which leak into subsurface reservoirs from the surface, pollute groundwater, thus affecting drinking water. As a result, developing innovative AC-based materials to eliminate them from water is critical.

2.1.1. Orange, Mandarin, Banana Husks

In a study by Hashem and Amin, ACs from three different peels were prepared under different drying conditions, by sun or oven [46]. The activation agent was sulfuric acid, and the removal of methylene blue (MB) was examined. The results showed that all materials had acidic functional units on their surfaces, making them favorable for cationic dye adsorption, like MB. Drying fruit peels in an oven prior to treatment using H$_2$SO$_4$ reduced the total pore area and increased the average pore width. In comparison with the other fruit peels, AC derived from banana peels had the greatest elimination effectiveness, with a $Q_m = 810$ mg/g.

2.1.2. Orange Peels AC

Deshmukh et al. evaluated the adsorption of methyl red (MR) onto synthesized orange peel ACs by chemical activation with ZnCl$_2$ [47]. The key factors influencing the MR removal effectiveness that were studied were the MR concentration, adsorbent dose, solution pH, and adsorption temperature. The optimal conditions were found to be 60 min of contact time in an alkaline environment (pH = 11), while Langmuir demonstrated a better fit with $Q_m = 111.11$ mg/g, rendering the material capable of eliminating MR from wastewaters.

2.1.3. Orange Peel/Watermelon Rind AC

The synergetic effect of a mixture of orange peels and watermelon rinds for the fabrication of large-surface-area and effective ACs (OPWRAC) to eliminate crystal violet (CV) and methylene blue (MB) in wastewaters was examined by Hanafi et al. [48]. Activation was achieved using the chemical activator ZnCl$_2$ and a microwave oven. The BET equation revealed 661.3 m$^2$/g, and an N$_2$ isotherm indicated that the material was composed mainly of mesopores. The results exhibited that microwave-assisted ZnCl$_2$ activation played a significant role, providing a great degree of porosity and pore volume. From FT-IR analysis, it was clear that the adsorption mechanism of OPWRAC towards CV and MB included electrostatic forces, π–π stacking, pore filling, and H-bonding due to the O-H, C≡C, C=O, and C-O functional groups of the material. Based on the kinetic and equilibrium findings, the adsorption of CV and MB occurred by chemisorption. As a result, OPWRAC had a notable adsorption efficiency for both CV (137.8 mg/g) and MB (200.7 mg/g).

2.1.4. Cactus Fruit Peels AC

Little research has been conducted on the production of AC from cactus peels (ACCP) according to Akkari et al. [49], who tested ACCP for the removal of the cationic dye Basic Red 46 (BR46). H$_3$PO$_4$ was used as the activating agent, since it produces better AC with non-hazardous properties. The adsorption mechanism involves electrostatic interactions between ACCP’s negatively charged surface and the dye molecule’s cation at pH = 6. The results show that the compound had microporosity, with a harsh, uneven surface and a substantial specific surface area of 1288 m$^2$/g, making it ideal for BR46 elimination. Finally,
it had an adsorption capacity of 806.38 mg/g, and could be recycled up to four times with minimal loss of efficacy, making it ideal for cationic dye removal.

2.1.5. Pineapple Peel AC

Another interesting study was conducted by Rosli et al. utilizing pineapple peels (PiP) [50]. Pineapple peel activated carbon (PiPAC) was created by a two-stage pyrolysis technique, followed by a carbonization step and an activation step. First, the pineapple peels (PiP) were carbonized at 700 °C, and the char was soaked with KOH before being gasified with CO2. For the adsorptive evaluation, Remazol Brilliant Violet (RBV) was used as the model pollutant in batch experiments. BET analysis showed that the PiPAC had a surface area of 1160 m²/g and mainly consisted of mesopores. Also, because of the chemical activation process, KOH dissolved in water, producing potassium ions (K₂CO₃). As a result, they entered the gaps that formed on the PiP char, penetrating it and effectively increasing the pores. The PFO kinetic model suited the data better than the other models, and the ideal pH was discovered to be pH = 2, with a Qₘ = 74.86 mg/g. Lastly, the material showed excellent regeneration towards RBV for up to three cycles.

The adsorption mechanism of PiPAC-RBV is presented in Figure 1. As can be observed, PiPAC presented hydroxyl (O–H) and carboxyl (C–O) groups, and for this reason, there were three possible mechanisms and interactions that could be combined during the adsorption of RBV onto PiPAC, such as:

- Hydrogen bonding between the oxygen atom of the dye and the hydroxyl groups of the PiPAC;
- Electrostatic interactions between the aromatic ring of dye and the oxygen on the surface of the PiPAC;
- π-π interactions between the π-electrons of carbonaceous PiPAC and in the aromatic ring of the dye [50].

![SEM images of PiPAC and the possible mechanism of PiPAC–RBV dye](image)

**Figure 1.** SEM images of PiPAC and the possible mechanism of PiPAC–RBV dye [50] (reprinted with permission).

2.1.6. Pomegranate Peel AC

Surface modification of activated carbon may also increase its adsorption capability for the removal of pollutants. This could be accomplished by chemically modifying its surface or by introducing external compounds, thus increasing the quantity of active areas for adsorption. Thamer et al. introduced AC derived from pomegranate peel (PPAC), as well as modified PPAC with sulfo-units (S-PPAC) [51]. To produce PPAC, KOH was
used as the activating agent along with carbonization. Figure 2 illustrates the production of PPAC and S-PPAC. The sulfonation of PPAC was achieved by dissolving 5-sulfonate-salicylaldehyde sodium salt and mixing it with PPAC, so that S-PPAC was obtained by covalent bonding. N₂ isotherm and BET analysis showed that both materials had high surface areas: 1180.63 m²/g for PPAC and 740.75 m²/g for S-PPAC. As the model pollutant, crystal violet (CV) was used. The optimal pH was found to be 10, with a 100% removal for the modified derivative, maintaining a high removal even after 5 cycles. According to the isotherm data, the Freundlich model was the most suitable for explaining adsorption, whereas the Elovich model was the most appropriate for characterizing adsorption kinetics. The adsorption mechanism suggested that electrostatic attraction was the key driving factor. However, the effect of pH evaluation showed that pore-filling, hydrogen bonding, and π–π interactions were critical in the mechanism of adsorption.

Figure 2. Preparation and surface modification of PPAC [51] (no special permission is required to reuse).

Table 1 summarizes the described modified activated carbons from peels for dye removal, providing the major experimental conditions used. As depicted, in alkalic conditions, the maximum removal capacities were achieved in most of the cases, and the removal rates reached up to 100% by using only 0.5 g/L of S-PPAC material.

Table 1. Modified activated carbons from peels for dye removal.

<table>
<thead>
<tr>
<th>Material</th>
<th>Peels</th>
<th>Modification Agent</th>
<th>Dye</th>
<th>pH</th>
<th>Initial Conc. (mg/L)</th>
<th>Dosage (g/L)</th>
<th>Contact Time (min)</th>
<th>Adsorption Capacity (mg/g)</th>
<th>R%</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOS</td>
<td>Banana</td>
<td>H₂SO₄</td>
<td>MB</td>
<td>9</td>
<td>1000</td>
<td>1</td>
<td>1140</td>
<td>810.00</td>
<td>81</td>
<td>[46]</td>
</tr>
<tr>
<td>OPAC</td>
<td>Orange</td>
<td>ZnCl₂</td>
<td>MR</td>
<td>11</td>
<td>100</td>
<td>1</td>
<td>60</td>
<td>111.11</td>
<td>93</td>
<td>[47]</td>
</tr>
<tr>
<td>OPWRAC</td>
<td>Orange/watermelon</td>
<td>ZnCl₂</td>
<td>CV</td>
<td>10</td>
<td>20</td>
<td>1</td>
<td>35</td>
<td>137</td>
<td>91</td>
<td>[48]</td>
</tr>
<tr>
<td>OPWRAC</td>
<td>Orange/watermelon</td>
<td>ZnCl₂</td>
<td>MB</td>
<td>200</td>
<td>200</td>
<td>1</td>
<td>35</td>
<td>200.00</td>
<td>94</td>
<td>[48]</td>
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Table 1. Cont.

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<thead>
<tr>
<th>Material</th>
<th>Peels</th>
<th>ModificationAgent</th>
<th>Dye</th>
<th>pH</th>
<th>Initial Conc. (mg/L)</th>
<th>Dosage (g/L)</th>
<th>Contact Time (min)</th>
<th>Adsorption Capacity (mg/g)</th>
<th>R%</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACCP</td>
<td>Cactus</td>
<td>H₃PO₄</td>
<td>BR46</td>
<td>6</td>
<td>20–1000</td>
<td>1</td>
<td>180</td>
<td>806.38</td>
<td>90</td>
<td>[49]</td>
</tr>
<tr>
<td>PiPAC</td>
<td>Pineapple</td>
<td>KOH/CO₂</td>
<td>RBV</td>
<td>2</td>
<td>100</td>
<td>1</td>
<td>360</td>
<td>74.86</td>
<td>72</td>
<td>[50]</td>
</tr>
<tr>
<td>S-PPAC</td>
<td>Pomegranate</td>
<td>KOH</td>
<td>CV</td>
<td>10</td>
<td>300</td>
<td>0.5</td>
<td>210</td>
<td>785.53</td>
<td>100</td>
<td>[51]</td>
</tr>
</tbody>
</table>

2.2. Pharmaceuticals Removal

Pharmaceuticals are an important and quickly rising group of organic pollutants distinguished by their regular and frequent use. Compared to some other organic pollutants, they survive in the natural world for an extended period of time, and may accumulate at extremely tiny amounts (in the µg/L and ng/L range) [52].

2.2.1. Jackfruit Peels AC

Magesh et al. used jackfruit peels (JFP) to synthesize AC and eliminate ciprofloxacin from an aqueous environment [53]. The JFP were made into a pair of adsorbent materials. The first was made by treating it with H₃PO₄ and converting it into activated carbon, and the second was prepared by grafting JFP activated carbon with ZnO (ZJFP) via a sonication method. The modified AC had a fascinating removal of 99.8% at optimal conditions, which included pH = 6 at a dosage of 0.3 g/L. The kinetic data prove that the adsorption procedure consisted of chemisorption, and that ZJFP better fit the Freundlich isotherm model, indicating double-layer adsorption. Figure 3 presents the SEM images before and after adsorption.

![Figure 3](image-url)

**Figure 3.** (a) FESEM analysis of JFP before adsorption; (b) FESEM analysis of JFP after adsorption; (c) FESEM analysis of ZJFP before adsorption; (d) FESEM analysis of ZJFP after adsorption [53] (reprinted with permission).
2.2.2. Pomegranate Peels AC

The removal of carbamazepine was examined by Al-Ghoul et al. by employing activated carbon from pomegranate peels (AC-PGPs) [54]. Pomegranate peels were converted to AC by heating and using NaOH as an activating agent, and the final product was characterized. The adsorption behavior of carbamazepine was studied with batch experiments by evaluating the effects of pH, temperature, contact time, and initial concentration. FT-IR and pH experiments validated that the driving forces for adsorption were hydrophobic and \( \pi-\pi \) interactions, while the kinetic data demonstrated that the procedure was chemisorption. Lastly, the findings showed that, after 1 h of contact time, AC-PGPs could eradicate up to 96.5\% of the pollutant, rendering it a considerable candidate for an adsorbent of pharmaceuticals.

2.2.3. Plantain Peels AC

In a study by Dada et al., plantain peels were used to synthesize AC (PPAC), and were impregnated with ZnO in order to eliminate chloroquine [55]. The activation was performed chemically by utilizing \( \text{H}_3\text{PO}_4 \), and the grafting was carried out by \( \text{Zn(NO}_3\text{)}_2 \) along with calcination. In this way, the obtained product exhibited low ratios of ash, moisture, and volatile components, leading to a surface area of 273.4 m\(^2\)/g, according to Saer’s method. Based on FT-IR and pH effect evaluation, the adsorption involved electrostatic attraction, while SEM revealed the pore-filling with images before and after adsorption. The optimal conditions were found to be an initial concentration of 10 ppm at a 1 g/L dosage and 313 K, showing a 78.89\% efficiency.

2.2.4. Mangosteen Peel AC

Ciprofloxacin is a fluoroquinolone antibiotic that has been extensively utilized for the remediation of both human and animal infections in the past few years. Its presence in wastewaters is harmful to the ecosystem. Tran et al. suggested the use of adsorbent-based AC from mangosteen peels [56]. \( \text{ZnCl}_2 \) was selected for the activation, creating a great number of voids and a surface area of 419.85 m\(^2\)/g, thus increasing the porosity and removal of the pollutant. The adsorption data showed a spontaneous, endothermic, physical, and chemical adsorption, achieving a 98\% removal at pH 6 and an initial concentration of 50 ppm. The effect of pH revealed that the driving force for the adsorption was electrostatic attraction. Furthermore, as shown in Figure 4, regarding the SEM images, there was an obvious difference in the surfaces of MP and ACMP, with the second being smoother.

![Figure 4. SEM image of the MP (A) and ACMP (B) [56] (no special permission is required to reuse).](image)

2.2.5. Dillenia Indica Peels AC

Fadzail et al. examined the removal of naproxen using activated carbon from Dillenia Indica peels (DI-AC), activating them chemically with \( \text{H}_3\text{PO}_4 \) [57]. FT-IR and effect of pH analysis exhibited that the adsorption was conducted with electrostatic as well as \( \pi-\pi \) electron donor-acceptor interactions. The results better fit the Langmuir and Temkin isotherms, and a pseudo-second order model was used for kinetic analysis. The data indicate that sorption occurred as a monolayer and was governed by a chemisorption procedure. However, the time required for equilibrium was very long (480 min), and the
Q_m was only 10.76 mg/g. From the SEM images presented in Figure 5, it is noteworthy that the raw material had a rough surface. Furthermore, there were no pores discernible on the surface of the raw material (Figure 5a) in comparison to the activated carbon prepared in this study (Figure 5b).

![SEM images](image-url)

**Figure 5.** SEM images for (a) raw material; (b) activated carbon at magnification of x500 [57] (reprinted with permission).

### 2.2.6. Banana Peels as AC

Recently, banana peels were applied for the purpose of producing activated carbon as a tentative adsorbent for the removal of pharmaceuticals, specifically amoxicillin and carbamazepine, from wastewater. The activation of carbon was conducted using phosphoric acid (H₃PO₄), and carbonization occurred at 350 °C, 450 °C, and 550 °C [58]. For the produced BPAC, the optimum conditions were found to be a pH of 5, a dosage of 1.2 g/L, a contact time of 120 min, and an initial concentration of the pollutants' mixture of 25 mg/L at 25 °C. The maximum adsorption capacities for BPAC were found to be 393.70 mg/g for amoxicillin removal and 338.98 mg/g for carbamazepine.

In Table 2, the modified activated carbons from peels for pharmaceuticals removal are tabulated, and as shown, pH 6 was applied in many studies reviewed in this manuscript. The ZJFP material exhibited the maximum removal capacities and rates using only 0.3 g/L.

### Table 2. Modified activated carbons from peels for pharmaceuticals removal.

<table>
<thead>
<tr>
<th>Material</th>
<th>Peels</th>
<th>Modification Agent</th>
<th>Pharmaceutical</th>
<th>pH</th>
<th>Initial Conc. (mg/L)</th>
<th>Dosage (g/L)</th>
<th>Contact Time (min)</th>
<th>Adsorption Capacity (mg/g)</th>
<th>R%</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZJFP</td>
<td>Jackfruit</td>
<td>H₃PO₄</td>
<td>Ciprofloxacin</td>
<td>6</td>
<td>50</td>
<td>0.3</td>
<td>120</td>
<td>70.12</td>
<td>99.8</td>
<td>[53]</td>
</tr>
<tr>
<td>AC-PGPs</td>
<td>Pomegranate</td>
<td>NaOH</td>
<td>Carbamazepine</td>
<td>6.7</td>
<td>20</td>
<td>8</td>
<td>60</td>
<td>-</td>
<td>98</td>
<td>[54]</td>
</tr>
<tr>
<td>PPAC-ZnO</td>
<td>Plantain</td>
<td>H₃PO₄</td>
<td>Chloroquine</td>
<td>7.02</td>
<td>10</td>
<td>1</td>
<td>120</td>
<td>50.5</td>
<td>78.8</td>
<td>[55]</td>
</tr>
<tr>
<td>ACMP</td>
<td>Mangosteen</td>
<td>ZnCl₂</td>
<td>Ciprofloxacin</td>
<td>6</td>
<td>50</td>
<td>3</td>
<td>60</td>
<td>29.78</td>
<td>98</td>
<td>[56]</td>
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<tr>
<td>DI-AC</td>
<td>Dillenia Indica</td>
<td>H₃PO₄</td>
<td>Naproxen</td>
<td>5</td>
<td>-</td>
<td>0.4</td>
<td>480</td>
<td>10.76</td>
<td>-</td>
<td>[57]</td>
</tr>
<tr>
<td>BPAC</td>
<td>Banana</td>
<td>H₃PO₄</td>
<td>Amoxicillin</td>
<td>5</td>
<td>25</td>
<td>1.2</td>
<td>120</td>
<td>393.70</td>
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<td>[58]</td>
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<tr>
<td>BPAC</td>
<td>Banana</td>
<td>H₃PO₄</td>
<td>Carbamazepine</td>
<td>5</td>
<td>25</td>
<td>1.2</td>
<td>120</td>
<td>338.98</td>
<td>81.5</td>
<td>[58]</td>
</tr>
</tbody>
</table>

### 2.3. Heavy Metals Removal

With the flow of time, and in tandem with population expansion and rise in industry, there has been a jump in the quantity of industrial waste which may pollute the natural world. Water contamination caused by waste consisting of heavy metals is detrimental for human health [59].

#### 2.3.1. Pea Peel AC

To face the threat of As (III) and As (V), Sahu et al. suggested the use of magnetized carbon-based adsorbents with AC derived from pea peels [60]. The activation was physically carried out by pyrolysis at 500 °C (MPAC-500) and 600 °C (MPAC-600), with the latter having the better results. The evaluation was conducted with batch experiments,
and the parameters that were tested were sorbent dose, initial pollutant concentration, temperature, and contact time. BET analysis exhibited that MPAC-600 had 214.04 m²/g and was a meso-macroporous material. The active sites available on the surface of the adsorbent were responsible for the mechanism of As adsorption. Groups such as -OH, aromatic amines, -CO, -NO₂, COO⁻, and -C-N were present on the surface of the material before adsorption, and almost similar compounds were found following As adsorption. The cation As was drawn to the anion COO⁻ on the compound’s surface via electrostatic attraction. Surprisingly, the removal by of As (III) was exothermic, while the removal of As(V) was an endothermic procedure. The optimal adsorption conditions for both were found to be pH = 7 and a contact time of 300 min, for an adsorption capacity of 1.33 and 0.80 for As (III) and As (V), respectively.

2.3.2. Navel Orange Peel AC

Xiao et al. prepared a glycine functionalized activated carbon derived from navel orange peel (NOP), and chose Gd (III) as the model pollutant [61]. The activation of NOPs/Glycine occurred chemically, with H₃PO₄ and heating up to 500 °C. According to the BET results, grafting with glycine increased the specific surface area by almost 50%, up to 1523 m²/g. Glycine addition also considerably increased activated carbon’s Gd(III) adsorption ability, with a removal efficiency of 99% at pH = 7. The adsorption isotherms were compatible with the Langmuir isotherm model, and the material had an optimal adsorption capacity of roughly 48.5 mg/g.

2.3.3. Orange Peels-TiO₂ Modified AC

Modifying AC with functional groups can significantly enhance its adsorptive efficiency. Neisan et al. produced AC using orange peel (OP) and studied its removal efficiency for Cu (II) [62]. The activation was achieved with pyrolysis and CO₂, and they grafted TiO₂ nanoparticles onto OP by mixing them in DI water and sonication. This modification increased the surface area, and increased the adsorption capacity to 13.34 mg/g. The kinetics indicated that the optimum contact time was 216 min to reach equilibrium, and the adsorption process was chemisorption. As shown in Figure 6, the adsorbents OP-TiO₂ and DS-TiO₂ after their modification with TiO₂ NPs presented aggregates on the surfaces of the particles, while in the unmodified materials, they displayed smoother surfaces.

![Figure 6. SEM images of (A) AC-OP, (B) OP-TiO₂, (C) AC-DS, and (D) DS-TiO₂ [62] (reprinted with permission).](image-url)
2.3.4. Pea Peel AC

In a study by Sahlabji et al., pea peel AC was synthesized with the chemical activating agent ZnCl$_2$ in order to eliminate hexavalent chromium [63]. Chemical activation resulted in an outstanding 1299 m$^2$/g and a dense porous matrix consisting of micropores, as shown by BET analysis. The increased number of pores, along with the abundant active sites, as confirmed by FT-IR, provided the material with an adsorption capacity of 480 mg/g at a dosage of 0.75 g/L. The kinetic and isotherm data exhibited that the adsorption process consisted of chemisorption together with intra-particle diffusion. A possible adsorption mechanism may have involved electrostatic interactions between Cr (VI) and the hydroxyl groups of the adsorbent.

2.3.5. Banana Peel AC

Ramutshatsha-Makhwedzha et al. used a composite material comprising chitosan, Al$_2$O$_3$, and AC derived from banana peels [64]. Chemical activation with KOH and H$_2$SO$_4$ was carried out so as to acquire a higher surface and porosity, according to the literature. BET analysis showed that the adsorbent had a surface area of 140.4 m$^2$/g, while SEM and TEM revealed the binding microstructure morphology. The composite’s adsorptive capabilities were evaluated with Cd (II) and Pb (II), some of the tests investigating the effects of pH, contact time, and adsorbent mass. The driving force for the adsorption of these heavy metals was electrostatic attraction, in agreement with the kinetics, which revealed that the process consisted of chemisorption.

According to the results shown in Table 3, all the applied materials showed very high removal rates, except for As removal. In detail, an adsorption capacity of 480.5 mg/g was found in the case of Cr(VI) by applying only 0.75 g/L of pea peel AC, but for As removal, the relative capacities were found to be only 0.8 mg/g and 1.3 mg/g for As(V) and As(II), respectively. It is worth noting that the initial concentration used in each case was different (400 mg/L and 0.5 mg/L for Cr(VI) and As, respectively), which also affected the adsorption capacity. The % removal rates were nearly 100 in the majority of them.

Table 3. Modified activated carbons from peels for removal of heavy metals.

<table>
<thead>
<tr>
<th>Material</th>
<th>Peels</th>
<th>Modification Agent</th>
<th>Heavy Metal</th>
<th>pH</th>
<th>Initial Conc. (mg/L)</th>
<th>Dosage (g/L)</th>
<th>Contact Time (min)</th>
<th>Adsorption Capacity (mg/g)</th>
<th>R%</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPAC-600</td>
<td>Pea</td>
<td>Pyrolysis</td>
<td>As(III)</td>
<td>7</td>
<td>0.5</td>
<td>3.0</td>
<td>300</td>
<td>1.33</td>
<td>87.6</td>
<td>[60]</td>
</tr>
<tr>
<td>MPAC-600</td>
<td>Pea</td>
<td>Pyrolysis</td>
<td>As(V)</td>
<td>7</td>
<td>0.5</td>
<td>2.5</td>
<td>300</td>
<td>0.80</td>
<td>99.7</td>
<td>[60]</td>
</tr>
<tr>
<td>NOPAC-Gly-60</td>
<td>Navel orange</td>
<td>Pyrolysis</td>
<td>H$_3$PO$_4$</td>
<td>7</td>
<td>50</td>
<td>0.6</td>
<td>90</td>
<td>48.5</td>
<td>99</td>
<td>[61]</td>
</tr>
<tr>
<td>OP-TiO$_2$</td>
<td>Orange</td>
<td>Pyrolysis-CO$_2$</td>
<td>Cu (II)</td>
<td>5</td>
<td>24.6</td>
<td>4.9</td>
<td>216</td>
<td>13.34</td>
<td>99.9</td>
<td>[62]</td>
</tr>
<tr>
<td>AC</td>
<td>Pea</td>
<td>ZnCl$_2$</td>
<td>Cr (VI)</td>
<td>1.55</td>
<td>400</td>
<td>0.75</td>
<td>180</td>
<td>480.05</td>
<td>99.5</td>
<td>[63]</td>
</tr>
<tr>
<td>BPAC-Al$_2$O$_3$-chitosan</td>
<td>Banana</td>
<td>H$_2$SO$_4$/KOH</td>
<td>Cd(II)</td>
<td>6</td>
<td>20</td>
<td>5.0</td>
<td>40</td>
<td>46.9</td>
<td>99.9</td>
<td>[64]</td>
</tr>
<tr>
<td>BPAC-Al$_2$O$_3$-chitosan</td>
<td>Banana</td>
<td>H$_2$SO$_4$/KOH</td>
<td>Pb(II)</td>
<td>6</td>
<td>20</td>
<td>5.0</td>
<td>40</td>
<td>57.1</td>
<td>99.9</td>
<td>[64]</td>
</tr>
</tbody>
</table>

2.4. Fluoride Removal

2.4.1. Sweet Lime Peel AC

Fluoride is a prominent hazardous contaminant found in both surface and groundwater. Siddique et al. faced this particular problem by utilizing sweet lime (Citrus limetta) to synthesize AC [65]. The activation was carried out physically via pyrolysis at two different temperatures, and the material with the highest treatment temperature (500 °C) showed the better results. The pH$_{ZPC}$ experiments revealed that the composites had more acid-active groups, making them ideal for anionic pollutant removal, while the increase in carbonization temperature came along with an increase in pH$_{ZPC}$. Particularly, the pH$_{ZPC}$ of AC-CLP$_{250}$, carbonized at 250 °C, was found to be 2.17, while the relative AC-CLP$_{500}$, carbonized at 500 °C, provided a pH$_{ZPC}$ value of 4.61, as Siddique et al. proved in their study. The adsorption data revealed that the favorable pH was 6.6 at a 1 g/L dosage and 240 min contact time, and isotherm studies showed that the Langmuir model fit better.
indicating a multilayer adsorption process. Finally, the mechanism of adsorption involved electrostatic attraction, since pH < pH_{ZPC}.

2.4.2. Banana Peel AC

A study by Getachew revealed the option of removing fluoride using H_{2}SO_{4}-activated banana peel AC [66]. The adsorption effectiveness was shown to be affected by working variables such as adsorbent dosage, contact duration, pH, and starting fluoride concentration. When applied to a real water specimen, the removal effectiveness ranged from 80 to 84%. With regard to the amount of time and adsorbent needed, banana peel AC seemed to have the slowest kinetics of all materials that were studied. At the optimal pH = 6.6, the exterior of the adsorbent was strongly protonated in the acidic media, and additional fluoride ions may have been adsorbed to the surface. In other words, the increased fluoride sorption rate in acidic media was due to a large coulombic force of attraction between the positively charged surface and the fluoride anion.

2.4.3. Pea Peel AC

Sahu et al. examined the removal of fluoride from an aqueous solution by both batch and column experiments with activated carbon derived from pea peels, activated by FeCl_{3} and pyrolysis [60]. The efficiency of MPPAC-500 was evaluated by the study of the effects of temperature, kinetics, and pH, and the material was characterized. In batch research, 5 mg/L starting fluoride concentration at a pH = 7, 4 g/L dosage and 420 min of exposure resulted in 99% fluoride elimination. The Freundlich isotherm model was preferred in the adsorption investigation, revealing a mono-layer adsorption process. The pseudo-second-order kinetic model accurately characterized fluoride accumulation, showing that chemisorption was preferred. Thermodynamic characteristics revealed that the adsorption reaction was endothermic and spontaneous. A possible adsorption mechanism is shown in Figure 7 below.

![Figure 7. Possible adsorption mechanism of fluoride on MPPAC-500 [60] (no special permission is required to reuse).](image)

In Table 4, the experimental conditions used for fluoride removal using activated carbons derived from fruit peels are shown.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>pH</th>
<th>Initial Concentration (mg/L)</th>
<th>Dosage (g/L)</th>
<th>Contact Time (min)</th>
<th>Capacity (mg/g)</th>
<th>R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPPAC-500</td>
<td>6.6</td>
<td>5</td>
<td>4</td>
<td>420</td>
<td>9.70</td>
<td>94.8</td>
</tr>
<tr>
<td>AC Banana</td>
<td>7</td>
<td>10</td>
<td>9</td>
<td>96</td>
<td>4.71</td>
<td>99</td>
</tr>
<tr>
<td>H_{2}SO_{4}</td>
<td>2</td>
<td>10</td>
<td>10</td>
<td>780</td>
<td>0.39</td>
<td>85</td>
</tr>
</tbody>
</table>

From the data presented, it is clear that the chemical activation of AC is a far better option regarding the efficiency of the adsorbents. During the activation process, these agents induced a material with an increased porosity and a higher number of pores, as mentioned in previous studies. However, every chemical modification agent can be specialized based on what properties are the most appropriate for each material. For instance, ZnCl_{2} presented denser and larger pores, as confirmed by SEM images of the
aforementioned AC materials, while H$_3$PO$_4$ showed higher specific surface areas, according to BET analysis. Nevertheless, these details affected the adsorption capacity and the kinetics of the process, leading to huge differences even with the same precursor materials.

Table 4. Modified activated carbons from peels for fluoride removal.

<table>
<thead>
<tr>
<th>Material</th>
<th>Peels</th>
<th>Modification Agent</th>
<th>pH</th>
<th>Initial Conc. (mg/L)</th>
<th>Dosage (g/L)</th>
<th>Contact Time (min)</th>
<th>Adsorption Capacity (mg/g)</th>
<th>R%</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-CLP 500</td>
<td>Lime</td>
<td>Pyrolysis</td>
<td>6.6</td>
<td>5–30</td>
<td>1</td>
<td>240</td>
<td>9.70</td>
<td>94.8</td>
<td>[65]</td>
</tr>
<tr>
<td>Banana-AC</td>
<td>Banana</td>
<td>H$_2$SO$_4$</td>
<td>2</td>
<td>10</td>
<td>96</td>
<td>780</td>
<td>0.39</td>
<td>85</td>
<td>[66]</td>
</tr>
<tr>
<td>MPPAC-500</td>
<td>Lime</td>
<td>FeCl$_3$</td>
<td>7</td>
<td>5</td>
<td>4</td>
<td>420</td>
<td>4.71</td>
<td>99</td>
<td>[60]</td>
</tr>
</tbody>
</table>

Grafting AC with other functional groups or linking it with a polymer appeared to have a positive outcome. These extra units can enhance the adsorption efficiency significantly, either by increasing the adsorption capacity or by making the composite available for the adsorption of different types of pollutants. Another interesting finding is that there is not extensive research in the field of fluoride removal by AC derived from peels, with only three research articles available in the past years.

3. Peels as Natural Adsorbents

Fruit peels as adsorbent materials, without previously being converted to activated carbon, have been used in the recent literature, but not in a large volume of publications. In particular, it has been found that they are extensively used mainly for the removal of heavy metals and dyes from wastewater, but there are no extensive reports on this type of agricultural waste in terms of pharmaceuticals or fluoride ions. A reference is made below to the relevant literature, and the research presented is classified according to the use of peels for the removal of organic and inorganic pollutants.

3.1. Organic Pollutant Removal

3.1.1. Pharmaceuticals Removal

In the study of Bouallegue et al. [67], a biosorbent from pomegranate peels (PG) was produced for the removal of sulfasalazine (SSZ), a pharmaceutical used to treat diseases such as rheumatoid arthritis and Crohn’s disease. According to the results, maximum removal (100%) was achieved at pH 4.8, with 50 mg/L as the initial concentration of SSZ and an adsorbent dose of 0.5 g/L within 60 min. The Langmuir model was found, according to isotherm models, to best describe the adsorption process, suggesting a monolayer, homogeneous surface. In addition, Elovich and intra-particle models recommended more than one mechanism taking place in the adsorption process. Thermodynamics exhibited a spontaneous and endothermic process. Therefore, pomegranate peels appear to be an auspicious adsorbent for the treatment of pharmaceutical wastewater [67].

Furthermore, banana peel (BP) was studied to remove acetylsalicylic acid (ASA), an analgesic and anti-inflammatory drug in aqueous solution [68]. The results exhibited that BP had a satisfactory maximum adsorption capacity of 2.29 mg/g, according to the Langmuir model. pH 3.0 was found to be more efficient in removing ASA, but in this study, pH 7.0 was chosen for further experiments, as it is the value used in water treatment plants in Brazil [68]. A dosage of 1.5 g of adsorbent was the optimum applied to achieve a maximum removal of around 48% at only 15 min of contact time. After this time, a decrease in the drug adsorption was observed, probably due to the desorption of ASA from the BP during agitation and due to the weak interactions between the drug and the banana peel.

3.1.2. Dye Removal

Regarding dye removal by natural fruit peels, recent studies are summarized as follows. Particularly, banana peels were used to remove 75.3% of Congo Red by using an
initial concentration of 20 mg/L and by applying 18.8 g/L of adsorbent at pH 10 for 90 min as the contact time. According to kinetics, the best model found to fit the experimental results was the pseudo-second order. Isotherm data showed an adsorption capacity of 1.727 mg/g, according to the Langmuir model, at 313 K [69].

Moreover, Ahmed et al. [70] used 2.0 g/L of orange peels to remove 86.7% of 50 mg/L crystal violet. A pH of 8.0 was used, and at 303 K, the Langmuir model was best fitted to the results presenting a Q_{max} = 138.9 mg/g. Equilibrium was reached at 70 min, and according to kinetics, the adsorption was better described by the pseudo-second order model.

Very recently, banana, orange, and pomegranate peels were applied as natural adsorbents for the removal of both anionic and cationic dyes from wastewater [25]. A descriptive and comparative report is made in this study, and the results show that these peels are very efficient materials for all the dye categories studied. Specifically, Reactive Red 120 (RR120), Reactive Black 5 (RB5), and Remazol Brilliant Blue R (RBBR) as anionic dyes, as well as cationic Methylene Blue (MB), were examined. The results showed that, for anionic dyes, 5.0–6.0 g/L of banana or orange peels was sufficient to remove more than 90% of anionic dyes at pH 2.0, and for cationic MB dye, 4.0 g/L was adequate to achieve 98% removal at pH 9.0. Pomegranate peels were efficient mainly for cationic dye. Finally, this study demonstrates the viability of reusing the banana, orange, and pomegranate peel adsorbents for eight, four, and five cycles, showing a gradual reduction of around 50% in their effectiveness [25].

Recently, pristine kiwi peel (KP) and nitric acid-modified kiwi peel (NA-KP) were produced as adsorbents and examined for the removal of cationic dyes from wastewater as malachite green (MG). According to the results, the adsorption process of MG onto both KP and NA-KP fit better to the pseudo-second-order kinetic model, but according to isotherms, the adsorption onto KP followed the Langmuir model, while the adsorption process of MG onto NA-KP followed the Freundlich isotherm model. In addition, the Langmuir maximum adsorption capacity for NA-KP was 580.61 mg/g, and for KP, it was 297.15 mg/g. This significant difference in the adsorption capacity of NA-KP compared to KP can be attributed to the increase in functional groups after HNO\textsubscript{3} modification.

In Table 5, the experimental conditions used for the removal of pharmaceuticals and dyes from wastewater are tabulated.

### Table 5. Modified fruit peels for organic pollutant removal.

<table>
<thead>
<tr>
<th>Material</th>
<th>Peels</th>
<th>Modification Agent</th>
<th>Organic Pollutant</th>
<th>pH</th>
<th>Initial Conc. (mg/L)</th>
<th>Dosage (g/L)</th>
<th>Contact Time (min)</th>
<th>Adsorption Capacity (mg/g)</th>
<th>R%</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG</td>
<td>Pomegranate</td>
<td>Untreated</td>
<td>Sulfasalazine</td>
<td>4.8</td>
<td>50</td>
<td>0.5</td>
<td>50</td>
<td>134.04</td>
<td>100</td>
<td>[67]</td>
</tr>
<tr>
<td>BP</td>
<td>Banana</td>
<td>Untreated</td>
<td>Acetylsalicylic acid</td>
<td>7.0</td>
<td>100</td>
<td>1.5</td>
<td>15</td>
<td>22.9</td>
<td>48</td>
<td>[68]</td>
</tr>
<tr>
<td>BP</td>
<td>Banana</td>
<td>Untreated</td>
<td>Congo Red</td>
<td>10.0</td>
<td>20</td>
<td>18.8</td>
<td>90</td>
<td>1.73</td>
<td>75</td>
<td>[69]</td>
</tr>
<tr>
<td>OP</td>
<td>Orange</td>
<td>Untreated</td>
<td>Crystal Violet</td>
<td>8.0</td>
<td>50</td>
<td>2.0</td>
<td>70</td>
<td>138.90</td>
<td>87</td>
<td>[70]</td>
</tr>
<tr>
<td>BP</td>
<td>Banana</td>
<td>Untreated</td>
<td>Anionic dyes</td>
<td>2.0</td>
<td>300</td>
<td>5.0</td>
<td>90</td>
<td>58.1</td>
<td>100</td>
<td>[25]</td>
</tr>
<tr>
<td>OP</td>
<td>Orange</td>
<td>Untreated</td>
<td>Anionic dyes</td>
<td>2.0</td>
<td>300</td>
<td>6.0</td>
<td>90</td>
<td>40.1</td>
<td>92</td>
<td>[25]</td>
</tr>
<tr>
<td>PP</td>
<td>Pomegranate</td>
<td>Untreated</td>
<td>Methylene Blue</td>
<td>9.0</td>
<td>300</td>
<td>6.0</td>
<td>90</td>
<td>98.1</td>
<td>98</td>
<td>[25]</td>
</tr>
<tr>
<td>KP</td>
<td>Kiwi</td>
<td>Untreated</td>
<td>Malachite green</td>
<td>-</td>
<td>50</td>
<td>0.05</td>
<td>-</td>
<td>297.15</td>
<td>-</td>
<td>[30]</td>
</tr>
<tr>
<td>NA-KP</td>
<td>Kiwi</td>
<td>HNO\textsubscript{3}</td>
<td>Malachite green</td>
<td>-</td>
<td>50</td>
<td>0.05</td>
<td>-</td>
<td>580.61</td>
<td>-</td>
<td>[30]</td>
</tr>
</tbody>
</table>

#### 3.2. Inorganic Pollutants Removal

**3.2.1. Heavy Metals Removal**

Acrylonitrile-grafted banana peels have been used for the removal of chromium [71]. Graft copolymerization is used for improving the thermal, chemical, mechanical, and hydrogel properties while preserving their intrinsic characteristics. This intricate process involves grafting diverse monomers onto the backbones of naturally occurring polymers, a procedure induced through the application of chemical initiators. In the realm of water purification, cellulose emerges as a particularly cost-effective adsorbent for extracting metallic ions. Renowned as one of the planet’s most abundant natural and renewable polymers, cellulose is highly esteemed due to its economic feasibility and widespread
Numerous research endeavors have explored the use of both untreated and chemically treated banana peels for extracting toxic heavy metal ions from water and wastewater. In a recent work, raw banana peels initially treated with acid, alkali, and bleaching agents such as NaClO3 and H2O2 are investigated, following their functionalization by acrylonitrile. The grafted banana peels (GBPs) that were produced served a crucial role as adsorbents for extracting Cr(VI) from water. The increased adsorption capacity observed in chemically treated banana peels can be ascribed to the removal of lignin and pectin, which are viscous compounds. Furthermore, the introduction of the acrylonitrile side chain into the cellullosic framework played a pivotal role in augmenting its interaction with the molecules being adsorbed [73]. As shown in Figure 8, according to SEM images, lignin, pectin, and other viscous compounds cause the fibers to stick together (Figure 8A), but they are removed during chemical treatment (Figure 8B). The surface became smoother after the adsorption of Cr(VI) due to the fact that the pores and caves were occupied by Cr(VI) (Figure 8E,F).

Moreover, dragonfruit and passion fruit have been extensively studied. The cellular composition of these agricultural materials primarily comprises tannin, lignin, and cellulose, presenting significant potential for the absorption of heavy metal ions [74]. Sulfuric acid (H2SO4) is used as a modification agent in fruit peels for the removal of heavy metals. These adsorbents, after the adsorption of Cu(II), were darker than they were prior to any treatment.

Copper, a heavy metal frequently found in industrial effluents, poses toxicity to living organisms, necessitating effective wastewater treatment measures. The adsorption process
has been a focal point of extensive research aimed at addressing wastewater issues across multiple industries. There are a few conventional technologies for the retrieval of metals from wastewater, but the researchers have turned their attention to low-cost adsorbents such as fruit peels [74].

The carboxylate group present at the active site exhibits a strong adsorption capacity for Cu$^{2+}$ ions. Consequently, the fruit peel adsorbents possess a higher number of metal-binding active sites and more negatively charged surfaces. This characteristic enhances the retention of Cu$^{2+}$ ions on the surface, resulting in a higher percentage of Cu(II) removal. However, the adsorption mechanism for metal ions is influenced by various factors, including the solution’s pH and binding characteristics. In this research, the adsorption of Cu(II) was elucidated by considering the pH effect and employing FT-IR-based characterization techniques. These analyses supported the binding of Cu$^{2+}$ ions on fruit peels, where functional groups electrostatically interact with Cu$^{2+}$ and Cu(OH)$_2$. At higher pH values, copper hydroxides were precipitated on the surface of the peels [74].

In a recent study, orange peel waste (POP) was effectively examined for its ability to remove Mn(II) and Co(II) ions from water [75]. For Co(II) ions, the addition of 0.2 g/L of POP at an initial concentration of 250 mg/L at pH 6.05 was found to be effective, with 100 min as the contact time. In the case of Mn(II) ions, an initial concentration of 200 mg/L was used by adding 0.2 g/L of the adsorbent at a lower pH of 5.42. The maximum adsorption capacities were found for Co(II) 25.91 mg/g and for Mn(II) 25.25 mg/g at 318 K. Furthermore, the pseudo-second-order model better fit the experimental data for both Co(II) and Mn(II) ions [75].

3.2.2. Fluoride Removal

One of the main waste products in tropical areas is banana peels. Regarding the removal of fluoride from this waste, there is no information. This has led scientists to investigate the adsorption of F$^-$ using banana peels [76]. The maximum adsorption of fluoride occurs at pH 6.0 (<pH$_{ZPC}$); thus, F$^-$ is more attached to the surface of banana peels having been chemically treated with Ca$^{2+}$. To determine the types of functional groups included in banana peels, the FTIR spectra were acquired. Many peaks were visible in the FTIR spectra, suggesting that the adsorbent is complex. –OH stretching, C–H stretching of alkane, C–H and C=O stretching of carboxylic acid or ester, COO–anion stretching, OH bending, C–O stretching of ester or ether, and N–H deformation of amines were the explanations given for bands that appeared at 3905.88–3258, 2928.13, 2856.01, 1734, 1631, 1393.45, 1269.11, and 1116.24–624.66 cm$^{-1}$, respectively. Among these, hydroxyl and carboxylic groups were crucial in the elimination of fluoride ions [76].

Furthermore, banana peels were modified by zirconium (IV), and the Zr(IV)-loaded saponified banana peels appeared to be an excellent substitute [77] for fluoride removal. Sorbents have recently been developed using rare earth metal oxides and hydroxides, such as zirconium. When it comes to species that contain oxygen donors, the zirconium (IV) cation exhibits strong electrostatic and coordination affinity. Additionally, Zr(IV)-modified adsorbents are non-toxic to humans and have a low leaching rate. In these conditions, pomegranate peel has been modified with Zr(IV) to improve its adsorption performance. Peels are often saponified—that is, treated with a basic solution—prior to Zr(IV) loading. By breaking the ester bonds and obtaining additional carboxyl and hydroxyl groups for Zr(IV) loading, this pretreatment (saponification) will be helpful in increasing the adsorption capacity [78].

Low adsorption occurs at pH < 2 because the combination of F$^-$ ions and H$^+$ ions in solution forms weakly ionizable hydrofluoric acid, which reduces the availability of F$^-$ ions for adsorption. The greatest fluoride adsorption onto Zr(IV)-SBP is observed at a pH of about 3. When Zr(IV)-SBP is protonated at this pH, the coordinated hydroxyl ligand in the coordination sphere of the loaded Zr(IV) interacts with the fluoride anion through coulombic interaction, leading to fluoride adsorption and the release of water. Fluoride anions and hydroxyl ligands exchange ligands to produce a net reaction. As the pH rises,
the fluoride adsorption gradually decreases, possibly as a result of competition between the increased concentration of hydroxyl ions and fluoride ions [77].

In Table 6, the experimental conditions used for the removal of heavy metals and fluoride ions from wastewater are summarized.

**Table 6. Modified fruit peels for removal of inorganic pollutants.**

<table>
<thead>
<tr>
<th>Material</th>
<th>Peels</th>
<th>Modification Agent</th>
<th>Heavy Metal</th>
<th>pH</th>
<th>Initial Conc. (mg/L)</th>
<th>Dosage (g/L)</th>
<th>Contact Time (min)</th>
<th>Adsorption Capacity (mg/g)</th>
<th>R%</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylonitrile grafted banana peels</td>
<td>Banana</td>
<td>Acrylonitrile (grafting)</td>
<td>Cr(VI)</td>
<td>3</td>
<td>400</td>
<td>4</td>
<td>120</td>
<td>6.17</td>
<td>99.7</td>
<td>[73]</td>
</tr>
<tr>
<td>H₂SO₄ treated dragon/passion fruit peels</td>
<td>Dragon fruit</td>
<td>H₂SO₄</td>
<td>Cu(II)</td>
<td>4</td>
<td>100</td>
<td>0.25</td>
<td>180</td>
<td>92.59</td>
<td>99.2</td>
<td>[74]</td>
</tr>
<tr>
<td></td>
<td>Passion fruit</td>
<td>H₂SO₄</td>
<td>Cu(II)</td>
<td>4</td>
<td>100</td>
<td>0.25</td>
<td>180</td>
<td>121.95</td>
<td>99.6</td>
<td></td>
</tr>
<tr>
<td>Orange peels</td>
<td>Orange</td>
<td>NaOH and CaCl₂</td>
<td>Mn(II)</td>
<td>5</td>
<td>200</td>
<td>0.2</td>
<td>100</td>
<td>25.25</td>
<td></td>
<td>[75]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Co(II)</td>
<td>6</td>
<td>250</td>
<td>0.2</td>
<td>100</td>
<td>25.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca-impregnated banana peel dust</td>
<td>Banana</td>
<td>Ca²⁺</td>
<td>F⁻</td>
<td>6</td>
<td>10</td>
<td>1</td>
<td>180</td>
<td>39.5</td>
<td>99</td>
<td>[76]</td>
</tr>
<tr>
<td>Zr (IV) loaded banana peels</td>
<td>Banana</td>
<td>ZrOCl₂ 8H₂O</td>
<td>F⁻</td>
<td>3</td>
<td>10</td>
<td>2</td>
<td>300</td>
<td>36.02</td>
<td>99</td>
<td>[77]</td>
</tr>
</tbody>
</table>

4. Conclusions

In this review, focus is given to recent trends involving using low-cost agricultural wastes as adsorbents, such as modified peels and even the natural adsorbents or activated carbons derived from them, for the removal of several pollutants found in wastewater. Among them, pharmaceuticals dyes, heavy metals, and ions such as fluoride have been selected as pollutants in order to present and compare the efficiency of the application of low-cost agricultural wastes as adsorbents.

Activated carbon derived from peels appeared to be an effective solution. Biomass-based activated carbons present high removal efficiency, and for some kinds of pollutants, even reach 99.9% rates using only a small dosage; i.e., the pea peel AC examined for the removal of Cr(VI), which exhibited a very high adsorption capacity (480.5 mg/g) by applying only 0.75 g/L.

Moreover, fruit peels as adsorbent materials, without previously being converted to activated carbon, have not been extensively used in the recent literature for pharmaceuticals or fluoride ions, but have been used mainly for the removal of heavy metals and dyes from wastewater. Therefore, it is concluded that research should be focused on more applications of these natural sorbents from peels in wastewater treatment in order to reduce the cost of the whole process. A significant difference in the adsorption capacity of nitric acid-modified kiwi fruit peels (i.e., NA-KP) compared to unmodified kiwi peels (KPs) for the removal of cationic dyes was found (580.61 and 297.15 mg/g, respectively), and this can be attributed to the increase in functional groups after modification.

Overall, mainly banana peels, and then orange and pomegranate peels, were found to be the most common agricultural wastes applied as natural peels or peel-based activated carbons for the removal of the specific pollutants examined in this review.


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