Bio-sorbents, industrially important chemicals and novel materials from citrus processing waste as a sustainable and renewable bioresource: A review

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Highlights
- The waste is rich in many chemicals and can be utilized.
- The waste is transformed into biosorbents for removal of heavy metals and dyes.
- Limonene and organic acids are transformed into biodegradable polymeric materials.
- The waste is transformed into fibers, fabrics and 3D printed materials.
- The waste can generate bioelectricity and carbon nanodots for bioimaging.

Graphical Abstract

Abstract
Citrus waste includes peels, pulp and membrane residue and seeds, constituting approximately 40–60% of the whole fruit. This amount exceeds ~110–120 million tons annually worldwide. Recent investigations have been focused on developing newer techniques to explore various applications of the chemicals obtained from the citrus wastes. The organic acids obtained from citrus waste can be utilized in developing biodegradable polymers and functional materials for food processing, chemical and pharmaceutical industries. The peel microstructures have been investigated to create bio-inspired materials. The peel residue can be processed to produce fibers and fabrics, 3D printed materials, carbon nanodots for bio-imaging, energy storage materials and nanostructured materials for various applications so as to leave no waste at all. The article reviews recent advances in scientific investigations to produce valuable...
Introduction

Citrus is the largest fruit crop in the world with annual production exceeding 124.3 million tons worldwide. Upon consumption, approximately, 40–60% of the fruit is discarded as waste. Every year 110–120 million tons of citrus waste are generated worldwide from citrus processing industries creating huge challenges regarding pollution of land, soil, underground water table, and overall wet/semi-solid waste management [1]. Currently, most of the waste is not processed adequately and end up either consumed by animals as feed materials or dumped in landfills. Recently, many researchers have been involving extensive investigations in developing newer techniques to produce various important chemicals from the citrus waste and their applications, motivated by both environmental and economic aspects. The citrus waste is an inexpensive renewable resource for production of important chemicals, viz., bioactive molecules which can be obtained from extraction methods and utilized in food and pharmaceutical industries, and production of ethanol, biogas and fuels employing fermentation, physico-chemical and microbial processes [2–10].

Metal industries related to mechanical works and battery manufacturing carrying out electroplating and metal plating release heavy metals. Also, heavy amounts of poisonous dyes are released from pigments or printing industries [11]. The industries based on pigment and dyes generate waste effluent containing various dyes, such as methylene blue, xanthene compounds, oxazine compounds, azo dyes, methyl violet, and so on. Among various dyes, methylene blue ‘MB’ and heavy metal salts are the repeatedly used chemicals for dying fabrics (silk and wool) or wood. MB is a cationic dye extensively used in textile printing. The wastewater effluents from these industries contain significantly high amount of dyes, which are hazardous to the environment. It contaminates the water bodies, such as rivers, ponds, lakes, ditches and even the ground waters. These are toxic chemicals and cause severe health problems, e.g., nausea, vomiting, diarrhea, abdominal and skin diseases when ingested. Thus, removal of dyes from wastewater is a serious concern not only from environmental point of view, but also, for the sake of human life. The popular methods for dye removal include adsorption of dye molecules onto suitable substrate, flocculation, precipitation of dye molecules, ion exchange, electro-kinetic coagulation, ionization, and so on. Among the above mentioned processes, adsorption of dye molecules has been observed an effective method due to its simple design, efficient in removal of low concentration contaminants, high adsorption rate, cost effective, and generates less byproduct at the end of adsorption [19]. Approximate price for the preparation of adsorbent from lignocellulosic biomass is around US$48/t; extraordinarily lower than its commercial alternatives, e.g., AC, (US$400–1500/t) [20]. Unlike carbonaceous materials (i.e., AC (Activated Carbon) and biochar), biosorbents are low energy-consuming materials because they do not require further pyrolysis process at high temperature.

Bhatti et al. (2010) used biosorbent derived from citrus reticulata waste biomass (CBW) for the removal of heavy metals, viz., Pb2+ and Co2+ from aqueous solutions. It was observed that the biosorption process was dependent on several parameters, such as, pH of the solution; dosage of the biosorbent employed; particle size of the biosorbent material; temperature of the solution medium; shaking speed during the entire experiment; contact time between the biosorbent and test media and initial concentration of metal ions. Recently, adsorbent with the magnetic properties has been designed for the removal of As. The magnetic properties of the bio-absorbent easily separated As from water by applying an external magnetic field [21]. Recently, Verma et al. (2019) has designed...
biosorbents with magnetic properties for the wastewater treatment. They synthesized biosorbent from Citrus limetta (peel and pulp) biomass waste at 500 °C temperature and carried out removal of As(III) and As(V) from aqueous solutions and groundwater samples [22].

The most popular adsorbent for eliminating heavy metals and dyes is activated carbon. However, its use is still limited because it is expensive in terms of its high operational cost [23–25]. Advance technology enables the scientists to have an attempt to reduce cost of treatment by using effective and readily utilisable adsorbents. Such inexpensive activated carbons can be obtained from agricultural wastes, e.g., wheat shells [26], rice husk [27], tea waste [28], neem leaf powder [29], cotton waste [30], banana peel, orange peel [31], and citrus peel wastes [21,32]. Citrus fruit peel is a readily available resource for making adsorbent materials. However, the sorption capacity of most of these biomass derived sorbents is generally low. The surface of these biosorbents can be modified to enhance the activity. Types of modification that can be introduced to the citrus waste biomass derived biosorbents are shown in Fig. 1.

Carbonization is one of the most favored methods for obtaining adsorbent material from citrus fruit peel. Weight ratio of the peel to activating agent, temperature and duration of carbonization are certain parameters for optimizing the preparation of an efficient adsorbent material [34]. Generally, the dried citrus fruit peel is fed to a mixer grinder and the grounded powder is mixed with activating agent, e.g., ortho-phosphoric acid or zinc chloride or sulfuric acid. This product is then, carbonized in a muffle furnace at an elevated temperature of ~450–500 °C up to a duration of 0.75–1.5 h. The weight ratio of the dried peel to activating agent varies in the range of 1:1 to 3:1. The charred product is then cooled and washed with dilute ammonia solution and distilled water. This removes any unconverted material from the carbonaceous activated carbon material. The washing is continued until the pH becomes neutral. The charred material is then left for drying overnight under ambient conditions. The dried samples are then crushed and fractioned into different sizes. These final different size samples are used for adsorption purposes. Recently reported research experiments on biosorption by citrus derived activated carbon are summarized in Table 1.

Organic acids, neo-hesperdin, limonene, and pectin derived chemical molecules and bio-based polymers

Complete biodegradation of a plastic bottle takes very long time of approximately 450–500 years. Biodegradation is decay or breakdown of a large complex molecule into small simpler units that are part of the cycle of life (O, CO2, H2O) by microorganisms, such as bacteria, fungi and algae under natural conditions within a considerable life time duration. Unless and until the plastics are recycled or managed judiciously, remains as visual displeasure, breeding ground for flies, microorganisms which causes bad odor, nuisance to soil flora and pollution to both, the underground water and environment. At present, the raw materials utilized for making packaging materials are obtained from fossil fuels. In recent years, the research for developing biodegradable polymers or plastics from renewable resources, such as starch, hemicelluloses, etc., that can replace the apparently non-biodegradable plastic materials. Starch, hemicelluloses and other polysaccharides are mostly obtained from plants. The annual starch production across the globe in 2015 is ~85 million tons and is expected to exceed 150 million tons by the year 2020 [59,60]. The demand for biodegradable plastics is increasing enormously. In 2011, approximately 0.85 million metric tons of biodegradable plastics were used. It is estimated to increase up to 6 million metric tons by 2019 [61,62]. According to Helmut Kaiser consultancy, the consumption of biodegradable plastics is expected to cover ~25–35% of the total plastic market by 2020 [62]. The main challenges in this direction are hydrophilic character of the plant starch or hemicelluloses materials, high retrogradation during storage time and poor mechanical strength. Retrogradation alters the crystallinity followed by alteration in the texture and color of the product material. This problem can be overcome by introducing the cross-linking between the various functional groups present on the surface of starch, e.g., hydroxyl groups responsible for water sensitivity or hydrophilicity. Cross-linking introduces the hydrophobic ester groups in the molecule and has been reported to improve the mechanical properties of the biodegradable polymers as well as reducing its hydrophilicity to a considerable extent. One of the very easily available cross-linking agents is citric acid which can be obtained commercially from citrus wastes as a by-product. Furthermore, limonene is

Fig. 1. Basic principle of surface modification of citrus waste derived biosorbent by chemical pre-treatment for the removal of pollutants; Adapted from the reference [33].
**Table 1**

Citrus waste derived biosorbent materials obtained from modification by heat/enzyme/chemical pre-treatments for the removal of toxic heavy metals and dyes from industrial effluent waters (BS – Biosorbent; BPT – Biosorbent Pre-treatment; BAT – Batch Adsorption Test; P.S – Particle size; q_{m} – Langmuir constant; maximum capacity of the monolayer adsorption (mg g^{-1}) meq g^{-1}; K_{f} – Freundlich constant; intensity of interaction between the sorbent and sorbate; Adsorption Isotherms: Not reported)

| Citrus waste part                      | Heavy metals/Dyes | Biosorbent pretreatment                                                                 | Results/Remarks                                                                 | Ref.  |
|---------------------------------------|-------------------|----------------------------------------------------------------------------------------|---------------------------------------------------------------------------------|-------|
| Peels (Citrus tamurana, Citrus latifolia, and Persian lime) | Nickel, Cadmium, Lead from Oriza sativa (rice) | Wash; Sundry; Grind, P.S. – 250 μm; **BPT**- (a) Soaking in 1% w/v citric acid for 10 min, drained, at 150 °C, 24 h- CTBS (Citric Acid treated BS) (b) CTBS heated to 400 °C, powdered-BSAC (BS Active Carbon) (c) BSAC treated with 1% w/v phosphoric acid, dried and sieved- ACPA (Active Carbon treated with Phosphoric Acid) **BAT**- 0.1 g CTBS, BSAC and ACPA added to 5 g of raw and rinsed rice, soaked in 250 ml DI with 2% NaCl at pH-6.3, 25 °C, 1 h | Maximum adsorption capacity order: Pb (-90%) > Cd (-90%) > Cu (-90%) > Ni (-75%) > Zn (-75%) > Al (-65%) Adsorption Isotherms:Langmuir: \( q_{m} (\text{mg g}^{-1})/K_{a} (\text{L g}^{-1})\) \( \text{Pb} (50.505/0.750); \text{Cu} (50.505/0.750); \text{Cd} (50.505/0.750); \text{Ni} (50.505/0.750); \text{Zn} (50.505/0.750); \text{Al} (50.505/0.750) \) Freundlich: \( K_{f}/n_{f} (\text{mg g}^{-1})/P_{b} (50.505/0.750); \text{Cu} (50.505/0.750); \text{Cd} (50.505/0.750); \text{Ni} (50.505/0.750); \text{Zn} (50.505/0.750); \text{Al} (50.505/0.750) \) | [35]  |
| Orange peel                           | Cadmium, Aluminium, Copper, Zinc, Nickel, Lead | Wash; Dry, 110 °C, 3d; Grind, P.S. – 0.074 mm; **BPT**-Heated at 250 °C, 350 °C and 450 °C @ 10 °C/min **BPT**-Protonation- 10 g dried peel soaked in 1L of 0.1 M HNO_{3}, stirred for 4 h at 120 rpm, 25 °C, rinsed with DI; Dried at 150 °C, 24 h- CTBS (Citric Acid treated BS) | Maximum adsorption capacity order: Pb (-90%) > Cd (-90%) > Cu (-90%) > Ni (-75%) > Zn (-75%) > Al (-65%) Adsorption Isotherms:Langmuir: \( q_{m} (\text{mg g}^{-1})/K_{a} (\text{L g}^{-1})\) \( \text{Pb} (50.505/0.750); \text{Cu} (50.505/0.750); \text{Cd} (50.505/0.750); \text{Ni} (50.505/0.750); \text{Zn} (50.505/0.750); \text{Al} (50.505/0.750) \) Freundlich: \( K_{f}/n_{f} (\text{mg g}^{-1})/P_{b} (50.505/0.750); \text{Cu} (50.505/0.750); \text{Cd} (50.505/0.750); \text{Ni} (50.505/0.750); \text{Zn} (50.505/0.750); \text{Al} (50.505/0.750) \) | [36]  |
| Orange peels                          | Cadmium, Copper, Lead | Wash; Sun dry, 6d; Grind, P.S. – 0.2 mm **BPT**-Protonation- 10 g dried peel soaked in 1L of 0.1 M HNO_{3}, 6 h; filtered, rinsed with DI; Dried to 65% dryness- CTBS (Citric Acid treated BS) | Maximum adsorption of Pb = 73.53 mg/g; Cu = 15.27 mg/g; Cd = 13.7 mg/g. Pb(99.5%) > Cu(99.5%) > Cd(99.5%) Adsorption Isotherms:Langmuir: \( q_{m} (\text{mg g}^{-1})/K_{a} (\text{L g}^{-1})\) \( \text{Pb} (73.53/12.5); \text{Cu} (73.53/12.5); \text{Cd} (73.53/12.5) \) Freundlich: \( K_{f}/n_{f} (\text{mg g}^{-1})/P_{b} (73.53/12.5); \text{Cu} (73.53/12.5); \text{Cd} (73.53/12.5) \) | [37]  |
| Orange peels                          | Lead, Cadmium, Zinc | Wash; Dry; Grind, P.S. – 1–2 mm; **BPT**-Protonation- 10 g BS in 500 ml 0.1 N HNO_{3}, stirred for 4 h at 120 rpm, 25 °C, rinsed with DI till pH = 4.0, dried at 45 °C for 12 h; PS = 1–2 mm- Protonated BS | Pb (58 mg g^{-1}) > Cd (44 mg g^{-1}) > Zn (20 mg g^{-1}) Adsorption Isotherms: Not reported | [38]  |
| Citrus paradisi (Grapefruit) peels    | Zinc, Nickel       | Wash; Dry, 50 °C till constant weight; Grind, P.S. 0.5–1.0 mm **BPT**-(a) Blocking – COOH group- 9.0 g BS suspended in 633 ml CH_{3}OH, and 5.4 ml HCl; stirred at 100 rpm, 6 h; Centrifuged, washed, freeze dried; (b) Blocking of –OH group- 5.0 g BS suspended in 100 ml HCHO, stirred at 100 rpm, 6 h; Centrifuged, washed and freeze dried | Native Peel BS- Ni^{2+}-1.331 meq g^{-1} (84.73%) Zn^{2+}-1.512 meq g^{-1} (92.46%) \( \text{COOH blocking reduces Ni}^{2+} \text{ sorption by 78.57%, Zn}^{2+} \text{ sorption by 73.31%} \) \( \text{OH blocking reduces Ni}^{2+} \text{ sorption by 22.63% and Zn}^{2+} \text{ sorption by 28.54%} \) Adsorption Isotherms:Langmuir: \( q_{m} (\text{meq g}^{-1})/K_{a} (\text{L mol}^{-1})\) \( \text{Ni}^{2+} (1.51/16.10); \text{Zn}^{2+} (1.51/16.10) \) Freundlich: \( K_{f}/n_{f} (\text{meq g}^{-1})/P_{b} (1.51/16.10) \) | [39]  |
| Citrus peel pectin                    | Lead               | Citrus peel pectins; (a) Low methoxylated (LM) pectin (methoxyl content 9%) and (b) High methoxylated (HM) pectin (methoxyl content 64%) **BPT**- 0.02 g BS in 200 ml MS; \( q_{m} = 0.1–1.0 \text{ meq g}^{-1} \) | Adsorption Isotherms: Not reported | [40]  |
| Citrus waste part | Heavy metals/Dyes | Biosorbent pretreatment | Results/Remarks | Ref. |
|-------------------|-------------------|-------------------------|----------------|-----|
| Citrus lemon      | Heavy Metals      | Wash; Dry, 80 °C, 24 h; Grind | Maximum adsorption capacity | 22 mg g⁻¹ adsorbent | [41] |
|                   | Cobalt            | BPT- Thermal activation in air at 500 °C, 1 h; Wash; dry, 100 °C, 24 h; PS: BS 150–200 | Adsorption Isotherms: Langmuir: \( q_m = \frac{q_m}{K_a} \) | | |
|                   |                   | BAT- 10 g/l BS; [Co²⁺] = 0–1000 mg/l; CT-10 h; SRs-200 rpm; pH = 6.0 | [25 °C (25.64/0.68 × 10⁴); 45 °C (14.97/3.90 × 10⁴)] | | |
| Orange waste      | Dyes              | Wash; Dry, 60 °C; Grind, Sieve- BS-100 mesh | Maximum adsorption capacity | | [42] |
| Peel (OP), Bagasse (OB), Peel-bagasse (OPB) | Lead            | BPT- 1 g BS + 20 m 0.1 M NaOH, agitation-2 h; Wash, dry-55 °C, 24 h; 1 g Modified BS + 8.3 ml 1.2 M Citric acid; agitation-30 min; filter; dry-55 °C, 24 h; heat-120 °C, 90 min; Wash; dry-55 °C, 24 h | Adsorption Isotherms: Langmuir: \( q_m = \frac{q_m}{K_a} \) | | [OP-(0.55/0.018); OMP-(0.85/0.012); OB-(0.40/0.012); OPP-(0.32/0.014)] | |
| Orange peels (OP), Lemon Peels (LP), Lemon based pectin peels (PP) | Cadmium         | Native orange and Lemon peels → Wash, Dry-38–40 °C, 12 h; Grind | Maximum adsorption capacity | | [43] |
|                   |                   | BPT- Protonation- Lemon based pectin peels are treated with 0.1 N HNO₃, 6 h; Dry for 12 h-38–40 °C; Wash, Dry; Grind-PS: 0.7–0.9 mm- Protonated pectin peels [PPP] | Adsorption Isotherms: Langmuir Isotherm: \( q_m = \frac{q_m}{K_a} \) | | [OP-(0.67/0.31); LP-(0.93/0.35); PPP, SAM: (Cd(NO₃)₂): (1.19/1.58)] | |
| Lemon Peel        |                   | Wash; Dry-60 °C, 24 h; Grind: PS-1 mm- RLP [Raw Lemon Peel] | Max. adsorption capacity | RLP – 20.83 mg g⁻¹ | [44] |
|                   | Cobalt            | BPT- 10 NP + 100 ml 2% IPA, 0.1 N NaOH, 0.1 N HCl, 0.1 N H₂SO₄, 0.1 N HNO₃; 4 h, 30 °C; Wash; Dry-60 °C, 24 h – ALP [Alkali Treated Lemon Peels] | ALP – 35.7 mg g⁻¹ | Adsorption Isotherms: Langmuir Isotherm: \( q_m = \frac{q_m}{K_a} \) | | [LP-(0.67/0.31); PPP, SAM: (Cd(NO₃)₂): (1.01/3.80)] | |
| Citrus limon juice| Mercury ion removal | GO (35 g) + Na₂S₂O₃ (64 mg) + 50 ml DI → Sonication, 1 h, Add 10 ml of Citrus limon juice and stand for 30 min; After equilibration, the mixture is sonicated for 5 min; Washed; Dried at 40 °C; Batch adsorption test were carried out at pH = 6–8 | Maximum adsorption capacity | | [45] |
|                   |                   | Sulfur loaded reduced graphene oxide nanohybrid: Particle size -20 nm | 90% Hg²⁺ removal in first 15 min. Complete removal in 30 min | Adsorption Isotherms: Langmuir Isotherm: \( q_m = \frac{q_m}{K_a} \) | | [907.74/0.0063] | |
|                   |                   | | Freundlich Isotherm: \( K_f = \frac{1}{n_f} \) | Freundlich Isotherm: \( K_f = \frac{1}{n_f} \) | [112.12/0.28] | |

(continued on next page)
| Citrus waste part | Heavy metals/Dyes | Biosorbent pretreatment | Results/Remarks | Ref. |
|-------------------|-------------------|-------------------------|----------------|------|
| **Citrus reticulata** | Acid Yellow-73 | | | |
| **Heavy Metals** | | | Maximum adsorption capacity | |
| | | | 96.46 mg g⁻¹ L⁻¹ | [46] |
| | | | Langmuir Isotherm: \( q_a (mg g^{-1})/K_a (L g^{-1}) \) | |
| | | | 96.46/0.006 ; \( R_s (0.769) \) | |
| | | | Freundlich Isotherm: \( K_f (mg g^{-1})/n_f L^n_f \) | |
| | | | 0.58/1.021 | |
| | | | **Dyes** | |
| | | | Congo Red (22.44/0.068) | |
| | | | Procion Orange (1.33/0.059) | |
| | | | Rhodamine B (3.23/0.049) | |
| | | | | | |
| **Heavy Metals** | | | Langmuir Isotherm: \( q_a (mg g^{-1})/K_a (L g^{-1}) \) | |
| | | | Maximum adsorption capacity | |
| | | | Congo Red | |
| | | | Acid Blue | |
| | | | Procion Orange | |
| | | | | | |
| **Congo Red** | | | Adsorption Isotherm: | |
| | | | Langmuir Isotherm: \( q_a (mg g^{-1})/K_a (L g^{-1}) \) | |
| | | | Maximum adsorption capacity | |
| | | | Congo Red (22.44/0.068) | |
| | | | Procion Orange (1.33/0.059) | |
| | | | Rhodamine B (3.23/0.049) | |
| | | | | | |
| **Congo Red** | | | Adsorption Isotherm: | |
| | | | Langmuir Isotherm: \( q_a (mg g^{-1})/K_a (L g^{-1}) \) | |
| | | | Maximum adsorption capacity | |
| | | | Congo Red (22.44/0.068) | |
| | | | Procion Orange (1.33/0.059) | |
| | | | Rhodamine B (3.23/0.049) | |
| | | | | | |
| **Grapefruit Peels** | Methylene Blue | | | |
| | | | Maximum adsorption capacity | |
| | | | Crystal Violet | |
| | | | | | |
| **Orange Peel** | Direct Yellow-12 | | | |
| | | | Maximum removal is 96% from 125 mg L⁻¹ of dye | |
| | | | concentration with adsorbent concentration of 5 mg L⁻¹ | |
| | | | Adsorption Isotherms: | |
| | | | Linear Langmuir Isotherm: \( q_a (mg g^{-1})/K_a (L g^{-1}) \) | |
| | | | Maximum adsorption capacity | |
| | | | Crystal Violet | |
| | | | | | |
| **Grapefruit Peels** | Crystal Violet | | | |
| | | | Maximum adsorption capacity | |
| | | | Crystal Violet | |
| | | | | | |
| **Pomelo Peel** | Methylen Blue (Cationic Dye); Acid Blue (Anionic Dye) | | | |
| | | | Maximum adsorption capacity | |
| | | | | | |
| **Orange Peel** | Direct Yellow-12 | | | |
| | | | Maximum removal is 96% from 125 mg L⁻¹ of dye | |
| | | | concentration with adsorbent concentration of 5 mg L⁻¹ | |
| | | | Adsorption Isotherms: | |
| | | | Linear Langmuir Isotherm: \( q_a (mg g^{-1})/K_a (L g^{-1}) \) | |
| | | | Maximum adsorption capacity | |
| | | | Crystal Violet | |
| | | | | | |
| **Pomelo Peel** | Direct Yellow-12 | | | |
| | | | Maximum removal is 96% from 125 mg L⁻¹ of dye | |
| | | | concentration with adsorbent concentration of 5 mg L⁻¹ | |
| | | | Adsorption Isotherms: | |
| | | | Linear Langmuir Isotherm: \( q_a (mg g^{-1})/K_a (L g^{-1}) \) | |
| | | | Maximum adsorption capacity | |
| | | | Crystal Violet | |
| | | | | | |
| Citrus waste part | Heavy metals/Dyes | Biosorbent pretreatment | Results/Remarks | Ref. |
|------------------|-------------------|------------------------|----------------|------|
| **Heavy Metals** |                   |                        |                |      |
| Citrus sinensis bagasse | Methylene Blue | Wash; Dry-60 °C, 72 h; Grind-PS: 0.25–0.75 mm BAT-0.1 g in 100 ml dye solution; [Dye] = 25–600 mg L⁻¹; CT-24 h; T = 30 °C; pH = 7.0 | Methylene Blue: (501.10/0.092) Acid Blue: (444.45/0.117) Linear Freundlich Isotherm: \( K_f (mg/g)C_0^{1/n_f} \) Methylene Blue: (65.94/2.033) Acid Blue: (72.87/2.323) Non-linear Freundlich Isotherm: Methylene Blue: (90.48/2.584) Acid Blue: (97.24/2.952) Maximum adsorption capacity 96.4 mg/g | [51] |
|   | Acid Blue | Langmuir Isotherm: \( q_m (mg/g) = K_a (L/mg)C_0 \) Methylene Blue: (112.36/0.0155) Acid Blue: (147.4/5.23/1.916) Maximum adsorption capacity 96.4 mg/g | | |
| Grapefruit Peel | Leather Dye mixture: Sella Solid Blue, Special Violet, Derma Bordeaux, Sella Solid Orange Cr(VI) | Wash; Dry-60 °C, 24 h; Grind-PS: < 0.5 mm BAT-0.3–1.5 g BS in 50 ml dye solution; [Dye] = 100–400 mg/l; pH = 5.5; T = 25 °C; SRs-120 rpm; CT = 24 h | Untreated Grapefruit peel BS → 45% for Dye mixture and 55% for Cr(VI) Modified Grapefruit peel BS → 80% for Dye Mixture and 100% for Cr(VI) Maximum capacity 1.1003 meq/g Maximum uptake Dye mixture 37.427 mg/g; Cr(VI) 39.06 mg/g Adsorption Isotherms: Langmuir Isotherm: \( q_m (mg/g) = K_a (L/mg)C_0 \) Dye mixture : 37.4270/0.0096 Cr(VI): 39.0628/2.8631 Freundlich Isotherm: \( K_f (mg/g)C_0^{1/n_f} \) Dye mixture: 2.40/3.80 Cr(VI): 76.6809/1.0887 | [52] |
| Orange peel | Congo Red,Methyl Orange | Wash; Sun dry-72 h; Grind BPT-(a) BS + 1% NaOH, EtOH; Filter; Wash, Air dry –OP (removal of lignin and pigments) (b) 10 g OP + 100 ml DI; Stirr and heat at 80 °C; 120 min; Cool to RT-Add N-vinyl-2-pyrrolidone-Stirr for 5 min-NVP/OP Copolymer (c) Transfer to glass tubes and irradiate with Gamma source –Radiation dose (10–50 kGy); dose rate-1.46 kGy/h- Cross-linked-NVP/OP Hydrogel; Wash; Dry | Maximum adsorption capacity Congo Red → 26 mg/g (pH = 7.0) Methyl Orange → 10 mg/g (pH = 6.0) Adsorption Isotherms: Langmuir Isotherm: \( q_m (mg/g) = K_a (L/mg)C_0 \) Congo Red: 75.0/0.03 Methyl Orange: 8.9/0.02 Freundlich Isotherm: \( K_f (mg/g)C_0^{1/n_f} \) Congo Red: 2.40/3.80 Methyl Orange: 3.07/1.14 Maximum adsorption capacity Congo Red: 11.62 mg/g Adsorption Isotherms: Langmuir Isotherm: \( q_m (mg/g) = K_a (L/mg)C_0 \) Congo Red: 11.62/0.0259 at 20 °C Freundlich Isotherm: \( K_f (mg/g)C_0^{1/n_f} \) Congo Red: 1.600/2.895 (at 20 °C) 1.879/5.261 (at 60 °C) Maximum adsorption capacity Congo Red: 11.62 mg/g | [32] |
| Citrus sinensis L | Remazol Brilliant Blue | Wash; Dry-60 °C, 24 h; Grind; Wash; Dry-60 °C; PS = 44–1180 μm BAT-300 mg BS in 30 ml dye solution; [Dye] = 30, 100,250 mg/l; SRs = 150 rpm; T = 20–60 °C; CT = 24 h | Maximum adsorption capacity | [54] |
| Citrus sinensis | Reactive Blue 19, | Wash; Dry; Grind-PS < 0.25 mm- Free BS (BS) BPT- (a) Immobilization: BS + Sodium alginate (1:2). The resultant beads preserved in 0.02 M CaCl₂ solution. - Immobilized BS (Im.BS) (b) 1 g BS + 5% glacial acetic acid; Wash after 1 h; Dry-70 °C, 24 h-Acetic acid treated BS | Maximum adsorption capacity Reactive Blue 19 Free BS → 37.45 mg/g Immobilized BS → 400.00 mg/g | [32] |

(continued on next page)
| Citrus waste part | Heavy metals/Dyes | Biosorbent pretreatment | Results/Remarks | Ref. |
|-------------------|------------------|-------------------------|----------------|------|
| **Heavy Metals**  |                  |                         |                |      |
|                   | (aaBS)           |                         |                |      |
| **BAT**           | 0.5–1.5 g in 50 ml dye solution; [Dye] = 50–300 mg/ml; CT = 60–120 min; pH = 2.0; T = 30 °C; SRs=100 rpm | Acetic acid treated BS → 75.19 mg/g |                |      |
|                   |                  |                         | Reactive Blue 49 |      |
|                   |                  |                         | Free BS → 135.16 mg/g |      |
|                   |                  |                         | Immobilized BS → 80.00 mg/g |      |
|                   |                  |                         | Acetic acid treated BS → 232.56 mg/g |      |
|                   |                  |                         | Immobilized BS |      |
|                   |                  |                         | Maximum adsorption capacity of 9.58 mg/g (95.89%) |      |
| **Lime Peel**     | Remazol Brilliant Blue R | Wash; Dry: 105 °C, 24 h; PS: 150 μm | Maximum adsorption capacity of 9.58 mg/g (95.89%) | [55] |
|                   | **BAT**          | 1–9 g BS in 50 ml dye solution; [Dye] = 10–50 mg/l; SRs=120 rpm; CT = 24 h; T = 27 °C | Adsorption Isotherms: Langmuir Isotherm: \( q_m = \frac{q_m g}{C_0 mg/l} / K_a (L mg g^{-1}) \); Freundlich Isotherm: \( K_f (mg g^{-1}) / n_f = \frac{1}{C_0 mg/l} \) |      |
| **Orange Peels**  | Acid violet 17   | Wash; Sun dry: 4 d; Grind; PS: 53–500 μm | Maximum adsorption capacity | [56] |
|                   | **BAT**          | 100–600 mg BS in 50 ml dye solution; [Dye] = 10 mg/l; pH = 2.0–10.0; CT: 80 min; T = 30 °C | Adsorption Isotherms: Langmuir Isotherm: \( q_m (mg g^{-1}) / K_a (L mg g^{-1}) \); Freundlich Isotherm: \( K_f (mg g^{-1}) / n_f \) |      |
| **Citrus limetta Peels** | Methylene blue | Wash; Sun dry: 4 d; Grind; PS: 80–200 BSS | Maximum adsorption capacity | [57] |
|                   | **BAT**          | 0.05 g in 25 ml dye solution; [Dye] = 25–250 mg/l; CT: 3 h; pH = 4.0 | Adsorption Isotherms: Langmuir Isotherm: \( q_m (mg g^{-1}) / K_a (L mg g^{-1}) \); Freundlich Isotherm: \( K_f (mg g^{-1}) / n_f \) |      |
|                   |                  | Optimum parameter: (87% removal at pH = 2.0 and 100% removal at pH = 6.27) Biosorbent concentration of 600 mg/50 ml and dye concentration of 10 mg L^{-1} | Maximum adsorption capacity: 227.3 mg/g; 98% removal |      |
| **Citrus sinensis Peels** | C.I. Direct Blue 77 dye | Wash; Dry: 105 °C; Grind; PS: 75–75 μm | Maximum adsorption capacity | [58] |
|                   | **BAT**          | 5–30 mg in 100 ml dye solution; [Dye] = 50 mg/l; pH = 2.0–12.0; SRs = 125 rpm; CT = 60 min | Adsorption Isotherms: Langmuir Isotherm: \( q_m (mg g^{-1}) / K_a (L mg g^{-1}) \); Freundlich Isotherm: \( K_f (mg g^{-1}) / n_f \) |      |
|                   |                  | Optimum parameters: pH = 4.0; Biosorbent particle size: 75 μ; Time to attain equilibrium: 30 min | Maximum adsorption capacity: 9.43 mg g^{-1}(59% removal) |      |
Another important chemical obtained from citrus wastes which has been found to generate biodegradable polymers.

**Organic acid based polymers**

A citric acid molecule contains multiple carboxyl functional groups capable of forming ester cross-linking between two or more molecules containing hydroxyl groups. In one such investigation by Seligra et al., in which starch obtained from cassava, glycerol and citric acid as a cross-linking reagent were treated at 75 °C yielding modified polymer with reduced retrogradation, decreased water vapor permeability up to 35% and stability up to 45 days [60]. Another research carried out by Azeredo et al. on hemicelluloses extracted from wheat straw, glycerol and citric acid yielded new polymeric material with improved water resistance and film like tensile properties. They also involved sodium hypophosphite in the reaction as a catalyst and concluded that there is no apparent effect of the catalyst on the properties of the final product [62]. Reddy et al. reported 150% enhancement in the mechanical properties of citric acid mediated cross-linked polymers compared with non-cross-linked films. The biodegradable polymer films cross-linked with 5% citric acid showed an improved stability. It underwent 35% loss under formic acid treatment for 5 h at 50 °C while the non-cross-linked films dissolved immediately indicating that

![Diagram of citric acid cross-linked biodegradable polymers from polysaccharides](image)

**Fig. 2.** (a) Citric acid cross-linked biodegradable polymers from polysaccharides; (b-c) Biopolymers and important chemicals derived from organic acids, viz., succinic acid and lactic acid [60,66].
citric acid mediated cross-linking may be utilized as an inexpensive as well as renewable mode of manufacturing biodegradable polymers and plastics [63]. The mechanism of citric acid cross linked biodegradable polymers derived from polysaccharides is shown in Fig. 2a.

Succinic acid polymerizes to form poly(3-allyloxy-1,2-propylene succinate and it finds possible use as a component of biodegradable bone cements. The terminal allyl groups present in the compound oxidizes into epoxy resulting in the formation of polyester-epoxy resins. The latter is used in the preparation of biodegradable bone implants. On the other hand, poly(ester-anhydride)s can also be synthesized from oligo(3-allyloxy-1,2-propylene succinate. The various aliphatic dicarboxylic acids are utilized to obtain versatile properties. The resultant poly(ester-
anhydride)s are utilized in the construction of microsphere polymer-drug systems and biomedical applications [64,65]. Succinic acid derived poly(butylene succinate) and poly(ethylene succinate) finds immense use in biodegradable alternative to many common plastics, such as, packaging field, films, bags, packaging boxes for both food and cosmetic products. Furthermore it is also used in manufacturing biodegradable tableware, medical articles, drug encapsulation matrices and implant materials, mulching films or controlled release material matrices for the release of pesticide and fertilizers in agricultural farms (Fig. 2b). Polyactic acid is obtained from lactic acid through a polycondensation reaction mechanism and the resultant is very fragile to be employed as packaging material. It is generally reinforced with other matrices to find versatile uses medical implants, scaffolds for bone and cartilage tissue engineering, etc. Various important chemical compounds derived from citric, succinic and lactic acids and their applications have been summarized in Fig. 2c.

Neo-hesperidin, limonene, and pectin based polymers

Pectins are multifunctional polysaccharides can be easily obtained from citrus processing waste (shown in Fig. 3a) and widely used in food industry as an emulsifier, gelling agent, stabilizer, and/or thickener. By the virtue of their diverse chemical structure they can interact with a number of different molecules to form novel materials with promising utilization in the pharmaceutical industry, controlled drug delivery matrices specifically colon targeted ones as these possess capacity to resist acidic conditions, health care and treatment. Neohesperidin [67], a highly valuable bioactive molecule obtained from citrus processing waste via extraction procedure [1,10] and can be transformed into hesperetin 7-glucoside (HG) employing a biotechnological process using bio-catalyst (commercial alpha-rhamnosidase) in the presence of rhamnose and further transformed into Hesperidin 7-O-glucoside (HGL) using lipase (Fig. 3a)[68]. The worldwide production of d-limonene is ~30–70 × 10³ tons. Limonene finds profound applications ranging from pharmaceutical to food industries. It can also be utilized in the production of green reagents and chemicals, e.g., p-cymene-2-sulphonic acid (p-CSA) and diverse range of brønsted acid ionic liquids (BAILs) as shown in Fig. 3b. BAILs thus derived are water immiscible and this property is not observed in sulfonic acid derived ionic liquids, therefore capable of synthesizing new materials and novel applications, e.g., catalytic hydrolysis of sucrose to an invert sugar syrup containing D-glucose and D-fructose in excellent yields [14,69]. P-cymene-2-sulphonic acid (p-CSA) have also been utilized for obtaining xylene, levulinic acid, and lignin from spent aromatic biomass [13]. A limonene molecule has two unconjugated electron rich alkenes or C=C double bonds with different degrees of substitution and this characteristic makes it a very effective molecule for radical polymerization [70–76]. One of the two C=C double bonds is an internal (endocyclic) double bond, i.e., 1-methyl-cyclohexane moiety, and another is a terminal (exocyclic) aliphatic bond. The latter is vinylidine or isopropenyl moiety. It is an optically active monoterpenic compound and occurs in large amounts in nature in stereochemically pure form: over 95% from orange peels [77]. The inherent property of the limonene molecule by the virtue of the intrinsic difference in the reactivity of the two unsaturated bonds enables it to form branched oligomeric thermostat precursor. The latter can be readily crossed-linked with a polythiol to form a d-limonene based poly-thioether network. Such thiol-ene coupling reactions returns high yields without significant influence of side reactions and helpful in generating bio-based thermostat polymers. It is reported that the thiol-ene coupling reaction at the exo-olefinic bond progresses about 6.5 times faster than the one present at the endocyclic C=C under solu-

Fig. 3. Schematic representation of (a) production of pectin, neohesperidin and limonene from citrus wastes, and (b–e) synthesis of important chemicals and novel biopolymeric materials [76,79–81,84].
tion condition [71]. Carbon dioxide is a naturally occurring renewable feedstock for preparing limonene based polymers. Limonene oil extracted from citrus peel wastes are oxidized into mono- as well as di-functional epoxides also called limonene mono- or di-oxide. The oxidized limonene is then introduced to copolymerization in the presence of carbon dioxide and a catalyst to yield thermoplastic polylimonene carbonate. The latter has been observed to possess the properties similar to that of polystyrene [78,79]. Robert et al. introduced a novel strategy for the synthesis of new biodegradable polyesters in terms of limonene based polyesters from copolymerization of limonene monoxide with dicarboxylic acid anhydride, such as succinic anhydride [80]. Furthermore, limonene dicarbonates synthesized from limonene dioxide and CO2 enables chemical fixation of 34% of carbon dioxide. Limonene dicarbonates when cured with polyfunctional amines, e.g., citric acid amides gives rise to a number of cross-linked terpene based green polyurethanes without involving any isocyanates, i.e., non-isocyanate oligo- and polyurethanes [81]. Most importantly, the production of polymers from limonene is an attempt to utilize the by-products obtained from citrus peel wastes and it does not interfere with food production. Auriemma et al. reported on co-crystallization of the regio- and stereoregular chiral copolymers polylimonene carbonate giving rise to higher melting points apparently arising from the higher levels of crystallinity and overall enhancement of polymer performance. The starting reactants are a cis-/trans- mixture of (R)- and (S)- limonene oxide and carbon dioxide. At room temperature and in the presence of a catalyst (diamine zinc complex), the reaction readily progresses with polymerization of trans- diastereomer of the limonene oxide leaving behind the cis- diastereomer unreacted, yielding highly regiodiastereo- and enantiomerically pure polymer, i.e., poly(R)- and poly(S-) limonene carbonate. The products are amorphous at this stage. An equimolar mixture of poly(R)- and poly(S)- limonene carbonate in n-hexane led to the formation of an intermediate which upon precipitation yielded a semi-crystallized stereocomplex (polylimonene carbonate) as final product. The resultant stereocomplex is a biodegradable polymer. This polymer, by the virtue of its properties, is anticipated to find use in biomedical applications, e.g., in drug delivery, tissue engineering and nanostructured bioactive surfaces [82]. Zuo et al., synthesized and studied the properties of luminescent films with tunable hydrophilic properties by natural-sunlight triggered thiol-ene chemistry involving d-limonene as a cross-linker agent. These newly developed films show very intense photoluminescence with high color specificity and purity when coated on commercially available UV-light emitting diode and illuminated under normal visible light [76]. The mechanism of formation of limonene derived novel polymers and functional materials have been summarized in Fig. 3(b)–(d).

Pectin exhibits good gelation, non-toxicity, high stability, and biocompatibility and can be obtained for a very low cost [69,83].
Pectin can be converted biochemically to aldaric acid. The latter, in turn, can be chemically converted to monomers for bio-based polyesters and polyamides. Aldaric acid is further converted to muconic acid. Muconic acid is a versatile monomer which can be converted to multiple polyamide monomers and a number of industrially important molecules and bio-based polymeric, such
Fig. 5. Schematic presentation of different uses of citrus processing wastes into valuable products, viz., (a) carbon nanodots from hydrothermal treatment of orange juice and orange peels and their applications in photocatalytic dye degradation in waste waters and (b) bio-imaging; (c) bioelectricity from electrochemically active microbial biofilm; (d) porous carbon materials for supercapacitor electrode material; (e) 3-D printed materials, (f) spun threads for making clothes (g) orange peel extract solution for polystyrene recycling and drug delivery, and (h) bio-inspired materials with excellent damping properties [106–108,110]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
## Table 2

Citrus waste utilization for the production of nanomaterials and their applications.

| Citrus                  | Synthesis Procedure                                                                 | Product                                      | Application                                      | Remarks                                                                 | Ref. |
|------------------------|--------------------------------------------------------------------------------------|----------------------------------------------|-------------------------------------------------|------------------------------------------------------------------------|------|
| Orange peel            | Wash, Sundry; Oven dry-150 °C, 10 h-Dried Specimen (Dsp) 1-2 g of Dsp + 100 ml 0.1 M H2SO4; rinse with DI; Filter; Dry-150 °C, 2 h; Soak in 60 ml Sodium hypochlorite at RT-4 h; wash till neutral pH; Hydrothermal treatment- 180 °C; Centrifuge; Dry-100 °C, 2 h II- 0.9 g ZnO + 0.1 g C-dots dispersed in 2-propanol and water; Stir-4 h; Filter, Wash, Dry-100 °C, 3 h | I-Fluorescent C-dots Yield-12.3%; II- C-dot loaded ZnO (10 wt% loading) Luminescent carbon dots: 400 mg CDs per 40 ml of juice; Particle size-1.5–4.5 nm | Bio-imaging                                                                 | [110]|
| Citrus nobilis dilicosa juice | Centrifugation-10,000 rpm | | | | |
| Pomelo peel            | Shred; Soak in boiling water; Hydrothermal treatment-180 °C-16 h; Wash; Freeze dry; Thermal annealing, 1000 °C, 2 h, NH3 | 3D connected porous hard carbon BET-1272 m²/g (Non-H₃PO₄ treated- 0.95 m²/g); pore size- 4-23 nm | Electrocatalyst for Vanadium redox couples in flow batteries | Enhanced electrical conductivity; B/N co-doping increase | [108]|
| Pomelo peel            | Clean; Freeze dry-2 d; Phosphoric acid treatment-24 h; Freeze dry-48 h; Carbonization-700 °C, 2 h, N₂; wash with hot water, dry-80 °C, 12 h | B/N-co-doped porous carbon incorporated with KetjenBlack nano-particles. BET surface area- 433.7 m² g⁻¹; Pore size- 5.4 nm | O-, P functionalized anode material for Sodium ion batteries | Cost effective | [7]|
| Orange peel            | Wash; Dry-60 °C, 24 h- Dried peel (DP) 3.0 g DP + 0.5 g KetjenBlack + 0.1 g Boric acid (99.5%) + 30 ml DI Stirred at 60 °C, 3 h, dry-60 °C, 24 h; Carbonization – 700–900 °C, 3 h, Argon atmosphere; Treatment with 3.0 M HCl-dry-60 °C, overnight- KB-BNPC | Citrus peel derived 3D-nanosheet of ~12 nm thickness; Pore size-1-5 nm; Surface area-1167 m² g⁻¹; C/O ratio-5.5; C/N ratio-34.3 | Cathode material for sodium ion storage | Good tolerance to MeOH poisoning | [103]|
| Citrus peel            | Wash; Chop; Soak-30 wt% KOH (95%)-30 min; Dry- 80 °C, 36 h; Pyrolysis-400 °C, 3 h, N₂ atmosphere; Wash with ETOH, Dry | 3D honeycomb like porous carbon; Specific surface area = 2725 m² g⁻¹; Pore size = 0.7–3.3 nm | Electrode material for supercapacitor | Cyclic stability up to 220 cycles; Capacitance of 181 mA h g⁻¹ at 200 mA g⁻¹. After 220 cycles, the capacity drops to 71 mA h g⁻¹ at 5 A g⁻¹ | [106]|
| Pomelo peels           | Carbonization followed by KOH activation | 3D-honeycomb like porous carbon; Specific surface area = 2725 m² g⁻¹; Pore size = 0.7–3.3 nm | Renewable carbon source in a mediatorless microbial fuel cell (MFC) | Electro-catalytic activity towards vanadium redox couples: onset potential and peak current; Facilitate adsorption and desorption of Vanadium ion by enhancing electron and mass transfer kinetics. | [104]|
| Orange Peel Citrus sinensis | Orange Peel waste- I-Blend in DI to make a juice; II- Dry-50 °C, 24 h, grind Microbial fuel cell containing anaerobic waste water in anodic chamber (orange peel waste) with graphite felt as anode; Aerobic air cathode chamber with platinum coated graphite cloth as cathode. GO (35 g) + Na₂S₂O₅ (64 mg) + 50 ml DI + Sonication, 1 h, Add 10 ml of Citrus limon juice and stand for 30 min; After equilibration, the mixture is sonicated for 5 min; Wash; Dried at 40 °C; Batch adsorption test were carried out at pH = 6–8 | Sulfur loaded reduced graphene oxide nanohybrid: Particle size ~20 nm | Bioelectricity generation | Maximum stable voltage of 0.59 ± 0.02 V at 500 Ω; Maximum current density = 847 ± 18.4 mA/m²; Maximum Power Density = 358.8 ± 15.6 mW/m² | [45]|
| Citrus limon juice     | Grind, Sieve; Particle size = 0.85–1.15 mm; Oven dry = 120 °C- Citrus biomass (CB) CB + NaOH (48, 120 °C, 20 min) → Delignified Citrus Biomass (DCB) DCB + Xac enzymes (Xanthomonas axonopodis pv. Citri strain 306 (IBSBF 1594))- 5 mg/g, 45 °C, 48 h → NaClO₂ (2%, 120 °C, 20 min) → Nanocellulose DCB + NaClO₂ (2%, 120 °C, 20 min) → Sonication in ice bath, 30 min → Nanocellulose | I- Nanocellulose from Enzymatic hydrolysis II-Nanocellulose from Chemical treatment | Nanocellulose with 55% crystallinity and average diameter of the nanocellulose fibers = 10 nm | Raw material for the preparation of high performance biodegradable nanocomposites | [99]|
| Citrus sinensis (L) osbeck Bagasse | | I- Nanocellulose from Enzymatic hydrolysis II-Nanocellulose from Chemical treatment | Nanocellulose with 55% crystallinity and average diameter of the nanocellulose fibers = 10 nm | Raw material for the preparation of high performance biodegradable nanocomposites | [99]|

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as adipic acid, terephthalic acid, hexamethylene diamine, caprolactam, caprolactone and 1,6-hexanediol. Polyamides are used in manufacturing engineering plastics, for example in automobiles. Pectin also shows versatile gelling properties and formation of complexes with other natural compounds and gives rise to a number of novel matrices useful in food and pharmaceutical industries. A summarized schematic presentation of pectin derived important chemicals and bio-based materials have been shown in Fig. 3e.

Micro- and nanocellulose

Microcrystalline cellulose is an important and valuable product obtained from citrus mesocarp. Contrary to cellulose, the microcrystalline cellulose (MCC) is a purified and partially depolymerized non-fibrous form of cellulose. It is white in color, odorless, tasteless and crystalline powder consisting of porous particles. MCC is widely used in pharmaceutical industries as a binder material or as diluents in oral tablets and capsule formulations. It can be utilized in many ways, viz., wet and dry formulations, direct compression processes, such as spheronisation and pelletisation, and so on [85–89]. MCC particles are porous and imbibe water to swell and disintegrate readily. This property supports tablet formulations, where the tablets are hard initially and easily disintegrates in water due to swelling. Citrus mesocarp is a good source of α-celluloses and the MCC can be extracted using HCl treatment on the same. Citrus mesocarp is first dried and pulverized to obtain powder form. This is then treated with 17.5% w/v 2.5 N HCl followed by digestion with 2% w/v NaOH at 80 °C for 3 h. The extracted cellulosic material thus obtained consisted 62.5% of α-cellulose and 25.3% of MCC [86]. MCC also possess lubricant and disintegrating properties, and therefore, utilized in cosmetics and food products especially for replacing fatty foods [90]. The wide applications of MCC in health related products are possible due to its physiological inertness which makes it stable and safe.

Nanocelluloses have greater surface area and high aspect ratios than macro or micro-cellulose fibers, making it a versatile and eco-friendly material for paper products of appreciable quality, cosmetics, pharmaceutical and food products as fat replacers or texturing agents, moldable light weight and high strength materials, materials for electronics, stabilizing agents for water based latex paints, coatings and suspensions [100]. The enzymatic extraction of nanocellulose is reported to be carried out using Xac enzymes obtained from the bacterial strain Xanthomonas axonopodis pv. citri strain 306 (IBSBF 1594). This bacterial strain is isolated from

| Table 2 (continued) |
|----------------------|
| Synthesis Procedure | Remarks |
| Wash; Dry; Grind and sieve 60 mesh size | Crystalline nanocellulose fibers with average diameter = 9.7 nm |
| Grounded peel (30 g) + toluene and Ethanol (2:1) – Soak overnight | Raw material for the preparation of high performance biodegradable nanocomposites |
| Grounded peel (30 g) + 10 ml DI water | Nanocellulose from Acid hydrolysis |
| Extracted Cellulose (EC) | Crystalline nanocellulose fibers with averagediameter = 9.7 nm |
| Crystalline nanocellulose fibers | Raw material for the preparation of high performance biodegradable nanocomposites |

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infected fruits which are fatal to the citrus crop. The enzymes help in specific digestion of orange fibers and obtaining nanocellulose [99,101,102].

**Novel materials**

**Energy storage materials**

3D structured porous hard carbonaceous materials prepared from simple pyrolysis of pomelo peels previously treated with H$_3$PO$_4$ at 700 °C in inert N$_2$ atmosphere when employed as an anode material for sodium ion batteries delivered a capacity of 181 mA h g$^{-1}$ at 200 mA g$^{-1}$ and a cyclic stability after 220 cycles retaining a capacity of 71 mA h g$^{-1}$ at 5 A g$^{-1}$[103]. Carbonaceous anode materials for sodium ion batteries have been found to deliver high capacity at inexpensive costs. Furthermore, its natural abundance and renewability is an added advantage. Phosphoric acid pre-treatment of the pomelo peels introduces functionalization of the carbonaceous material surface especially N- and O-containing functional groups. Further, pyrolysis helps in developing 3D porous structure of high surface area. The latter has been reported to improve the electrical performance of the carbon based sodium ion anode due to enhanced reactivity and electronic conductivity. The porous material possesses high surface area of ~1272 m$^2$ g$^{-1}$ along with active functional groups believed to support the Na$^+$ intercalation into the graphene layer and pseudocapacitive effect [103]. Another attempt by Liang et al. produced 3D honeycomb structured porous carbon (HLPC) via simplified carbonization process from pomelo peels pre-treated with KOH exhibiting a high specific surface area of 2725 m$^2$ g$^{-1}$. The porous carbon surface contain N- and O-containing functional groups and exhibited high specific capacitance of 342F g$^{-1}$ and 171F cm$^{-3}$ at 0.2 A g$^{-1}$; appreciable rate capability of 212 F g$^{-1}$ and 106 F cm$^{-3}$ at 20 A; and cyclic stability over 1000 cycles at 10 A g$^{-1}$ with 98% retention [104].

Nanoporous carbon nanosheets (NP-CNSs) developed by Raya et al. from citrus peels pre-treated with KOH (soaking 100 g citrus peels in 30 wt% KOH for 30 min and dried at 80 °C for 36 h followed by pyrolysis at 800 °C for 2 h in N$_2$ atmosphere) exhibited 50 times higher electrical conductivity (26 S cm$^{-1}$) than reduced graphene oxide. The material possessed high surface area of ~1167 cm$^2$ g$^{-1}$, doped with redox active hetero atoms, viz., O-, and N-containing functional groups and exhibited enhanced electrochemical performance in terms of high specific capacity of 140 mA h g$^{-1}$ at 0.1 A g$^{-1}$ in the cathodic potential range. The full cell symmetric supercapacitor device showed good cyclic performance over 100,000 repetitive cycles and stability over 2000 repetitive cycles [105]. A study on catalytic effects of boron and nitrogen co-doped porous carbon material obtained from orange peels integrated with Ketjenblack nanostructured particles for all vanadium redox flow battery showed enhanced activity towards V$^{2+}$/V$^{3+}$ and VO$^{2+}$/VO$^{3+}$ and improvement of redox onset potentials and peak currents. A B:N doping ratio of 0.65 has been found to exhibit good chemical stability and synergistic effect on the catalytic behavior. The defects on the surface of porous carbonaceous material obtained from citrus peels facilitate adsorption and desorption process of the vanadium ions (Fig. 5a) [106].

Bioelectricity from microbial fuel cell run on citrus peel waste can be explored as sustainable energy production from increasing piling up waste biomass. In one such study a microbial fuel cell run on a dual chamber mediator less orange peel waste generated a maximum voltage of 0.59 ± 0.02 V at 500 mA. Maximum power density of 558.8 ± 156 mW/m$^2$ and current density of 847 ± 18.4 mA/m$^2$. The microbial biofilm dominated by fermentative bacteria and exoelectrogens, viz., Enterococcus, Paludibacter and Pseudomonas (Fig. 5c) [107]. Citrus waste reuse for the production of nanomaterials for various applications has been listed in Table 2.

**Carbon nanodots**

Sahu et al. synthesized highly photoluminescent carbon dots with PL quantum yield of 26% from orange juice by hydrothermal route which demonstrated excellent results as a probe material in cellular imaging [108]. The carbon nanodots hence prepared are inexpensive to make. These are partially crystalline in nature and exhibit strong, stable and tunable photoluminescence dependent on excitation wavelength and pH. Also, these are non-toxic, substantially biocompatible and easily imbibed by the living cells for bio imaging (Fig. 5b). These demonstrated good bio compatibility as these are tolerable up to the concentration of 200 μg/ml and sustain long incubation durations up to 72 h. On the contrary, the CdSe quantum dots are reported to cause 76% reduction in cell viability with a concentration of 62.5 μg/ml and 24 h of exposure time [109]. Carbon nanodots synthesized from orange peel waste using hydrothermal carbonization method at 180 °C showed amorphous polyatomic hydrocarbons and large quantity of oxygen functional groups. Such carbon nanodots were composited with ZnO and experimented for developing effective photocatalytic system for the degradation of naphthol blue-black azo dye under UV-radiation and recoded for superior activity (Fig. 5d) [110]. Carbon nanodots possessed certain properties edge over semiconductor quantum dots, such as low toxicity, chemical inertness, easy functionalization and appreciable photoluminescence which make them preferable material for future nanodevices and applications like bioimaging, biosensors, light emitting diodes, and so on [110–113].

**Material for 3D printing**

The cellulose, hemicelluloses, pectin and proteins present in the citrus peels, like other organic celluloses, possess high tensile strength due to high molecular weight chain length of cellulose as well as high heat resistance due to its crystalline nature. Peel waste can be converted into a sustainable feed material for 3D printing (Fig. 5e). In one such report, the dried peels were crushed, blended and mixed with a suitable organic binder to obtain an appropriate combination of properties suitable to create 3D printed objects under the product name “APeel” [114]. Another similar research has been carried out by a team of research students at the Institute for Advanced Architecture of Catalonia (IAAC) in Spain with gelatine and orange peels combined with corn starch or silicone to obtain an appropriate composition sufficiently decent for creating 3D-printed objects under the project name Vivo/Bio-Plastica [115].

**Fibers and textile**

The cellulose extracted from citrus peel wastes by means of chemical extraction using H$_2$O$_2$ under basic conditions (pH = 11–12) is considered to be a highly inexpensive fiber material without using chlorine, unlike other cellulose extracting methods where chlorine is utilized. One of the probable reasons behind this is chlorine radicals might react with cellulose material to generate toxic organochlorine. After treating with H$_2$O$_2$, the solid cellulose material is filtered, washed with distilled water until the pH becomes neutral, and in the final step, with acetone and dried in oven. The final product is z-cellulose (>90 wt%) capable of being spun into fibers or threads [116]. Biku et al. incorporated two different pulp reagents, viz., sodium sulphite and sodium metabisulfite for cellulose extraction from orange peels followed by bleaching with hypochlorite and oxygen in order to achieve greater levels of purity. The product cellulose thus obtained showed low crystallinity, appreciable whiteness and better water retention capacity and reasonable molecular weights. These are anticipated to find applica-
tions in fillers, water absorbents, also as raw materials for cellu-
losic derivations [117]. Fibers obtained from citrus create a possi-
bility for obtaining textiles from sustainable renewable resources
(Fig. 5f). A creative start up for the commercial production and
manufacturing of garments from orange fibers has been installed
under the brand name “Vitamin Garments” by a team of entrepre-
neurs. The thought has been developed by the creative team that
vitamin garments are eco-friendly fabrics and believed to release
citrus active ingredients which are good for skin [116].

Green solvent for recycling polystyrene waste and material for
removal of oil spills from waste water

Orange peel extract obtained from processing waste exhibited
many interesting results, such as potential solvent for biopolymers,
such as gelatin, development of nanofibers and formulation for
drug delivery matrices, ink/print transfer medium and removal of
oil spills from waste waters. The orange peel extract upon standing
yields three distinct layers viz., bottom layer, middle layer and top
layer. Bottom layer has been explored as a solvent for biopolymers,
such as gelatin followed by electrospinning to obtain gelatin nano-
fibers and formulation of drug delivery matrices. The middle layer
of the extract possesses small sized cellulosic flakes. This part can
be pyrolyzed to obtain nano-structured hard carbon and employed
as an electrode material for rechargeable batteries. The top layer of
the extract has been demonstrated as a medium for recycling of
polystyrene waste. The latter transforms into sub-micron length
scale aligned fibers, hydrophobic and lyophilic in nature, capable
of absorbing oil spills as well as oil recovery with reusability up
to five times (Fig. 5g) [118].

Bio-inspired structures based on citrus peels

The peels of pomelo fruits (Citrus maxima) show hierarchical
structures enabling the fruit possess an impact resistance property
of considerable magnitude. A typical pomelo fruit weighs 1–6 kg
but withstands impact forces when dropped from a height of more
than 10 m and remains extremely undamaged. Pomelo peel or epi-
carp is 2–3 cm in thickness consists of outer epidermis or exocarp
(flavedo) containing oil glands and a spongy mesocarp underneath
consisting of air filled intercellular spaces. The aluminium hybrid
composite structures inspired from pomelo peel structured devel-
opled by Fisher et al., exhibited enhanced material properties in
terms of tensile strength (higher than aluminium) and ductility
(greater than aluminium-silicon alloy) and impact resistance
[119,120]. Furthermore, these newly developed materials were
lighter in weight and demonstrated greater load bearing capacity
as well as energy saving in making. The metal hybrid composite
structure consists of highly ductile pure aluminium wire core in
the center and high strength silicon alloy A 356 cast alloy in the
surrounding outer shell. These bio-inspired hybrid composite
materials are anticipated to provide promising properties for manu-
facturing safety devices as the applied stress energy can be effi-
ciently absorbed by means of fracture of the outer high strength
but less ductile A 356 cast alloy-shell and subsequently by the
deforation of the highly ductile aluminium inner core. In this
direction, B_{12},Si_{12} model alloy was also tested previously and
had been found to be excellent candidates to make bioinspired
structures [119]. Study on structure-function relationship of the
foam like pomelo peel for developing new materials with sufficient
robustness and capability of demonstrating high impact resistance
has also been reported by other groups [121]. The spongy contents
of the pomelo peels have also been attempted to design eco-
friendly loose filled foam structured packaging materials (Fig. 5h)
[122].

Conclusion

Citrus waste from processing industries have been increasing in
quantity every year with increasing demand for processed and
packaged food world-wide. With increasing population and reduc-
tion of habitable lands, the dumping of citrus wastes has become a
huge challenge because of environmental pollution and threat to
ecosystems. Researches related to waste management are now
focusing to find appropriate solution to this problem by developing
innovative techniques to convert citrus waste into important
chemicals and valuable products, via biological-/biochemical/che-
mical/physico-chemical/physical transformation. The biodegrad-
able polymers derived from organic acids find versatile utility
ranging from commodity products, human health and medical
management, overall reducing pollution to a substantial score. The
wet biomass can be energy materials for electrochemically active
microbial fuel cells, bio-imaging and energy storage materials.
Integrated research incorporating active coordination and collabora-
tion among farmers, citrus processing industries, transportation
systems and industrial researchers is the need of time to realize
the future of complete valorization of biomass so as to leave
behind zero waste for a greener and safer environment for our
future generation.

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Declaration of Competing Interest

All the authors hereby declare no conflict of interest.

Compliance with Ethics requirements

This article does not contain any studies with human or animal
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