

Review

Biotransformation of Citrus Waste-II: Bio-Sorbent Materials for Removal of Dyes, Heavy Metals and Toxic Chemicals from Polluted Water

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Abstract: Industrial processes and anthropogenic activities generate huge amounts of wastes in the form of chemicals, such as heavy metals, dyes, fertilizers, pharmaceutically active chemicals, battery effluents and so on. When these chemicals are left untreated and discarded in the ground or surface waters, they not only cause pollution and harm the ecosystem but also cause toxic effects on the health of human beings, animals and food crops. There are several methods of removal of these toxic materials from the wastewaters, and adsorption by bio-sorbents has been demonstrated as one of the most inexpensive, efficient and convenient methods. Citrus is one of the largest grown fruit crops in the tropical and subtropical regions on the planet. After processing of the fruits at food processing industries, approximately half of the fruit mass is discarded as waste, which causes a number of pollution problems. Alternately, this biomass can be converted to bio-sorbents for the removal of harmful and toxic chemicals from the industrial effluents and wastewaters. The first part of this article contains a thorough review on the biotransformation of citrus waste for the production of biofuel and valuable compounds by fermentation involving microorganisms. The second and concluding part reviews the recent progress in biotransformation of citrus waste biomass (that may be remaining post-extraction of valuable compounds/biofuel generation) into efficient adsorbent substrate materials and their adsorption capacities. The article also includes the details of the synthesis process and mechanisms of adsorption processes.

Keywords: citrus waste biomass; bio-sorbent; pre-treatment; heavy metals; dyes; activated carbon; batch adsorption; fixed-bed adsorption column

1. Introduction

Citrus is one of the most popular and largest cultivated fruit crops in the tropical and subtropical regions on the planet, with an annual turnover exceeding 110–124 million tons. The fruits are largely processed in the food processing industries, and approximately half of the fruit mass (45–55%) is discarded as waste. The discarded mass consists of peels

(flavedo and albedo), pith residue, seeds and parts inappropriate for human consumption. The waste, when directly discarded to the environment, causes huge problems in terms of pollution to the land and aquatic ecosystems, and underground as well as surface water resources. Alternately, this waste can be utilized as a sustainable and renewable natural resource and feedstock in a number of ways to obtain industrially important chemicals and valuable products by utilizing modern extraction methods, chemical processing techniques and biotransformation. On the one hand, utilization of the waste biomass provides an opportunity to produce valuable chemicals from green resources and avoid usage of harsh chemicals, and on the other hand, it helps in protecting the environment from the adverse effects of pollution. The authors have extensively reviewed the nature, properties and different technological processes of citrus waste valorization in their previously published articles [1–8].

1.1. Citrus Waste Pre-Treatment and Disposal

Citrus wastes produced by food processing industries are generally sent to waste-disposal plants, which require substantial transportation costs and availability of suitable sites for waste disposal. The most common waste management methods employed for the citrus wastes are composting, anaerobic digestion, incineration, thermolysis and gasification [9]. Commonly, in small processing units in the underdeveloped or developing countries, the wastewater is not believed to be toxic or harmful as sewage wastewater and is disposed of into drainage. When the dilute wastewaters, disposed of through drainage, reach streams, lakes, tidal waters, ponds or dumping wells, the organic solids carried by the wastewaters begin to decompose. During the process of decomposition, the dissolved oxygen present in the water is consumed. As a result, anaerobic or putrefaction reactions set in, and the aquatic organisms, such as insects, planktons (zooplanktons and phytoplanktons), fish, aquatic organisms, etc., die because of oxygen deficiency in the water [8]. Within the past three decades, there has been a multifold rise in the demand, and consequently, an increase in the production, supply, processing and applications of processed citrus products. At the same time, there has also been a huge rise in the quantities of dilute liquid and solid wastes, which are required to be disposed of appropriately. Large processing plants and units utilize large amounts of chlorinated waters to keep the processing tables, containers, vessels and equipment clean, and hence, the wastewater also contains chlorine. The effluent waters contain varied quantities of peel oil traces, pulp, juice sacs, follicles and organic materials [10]. Depending upon the concentration of materials and source of origin, the wastewater is divided into three categories, as follows:

- (a) Dilute wastewaters: This includes, (i) fruit-rinsing water, (ii) surface condenser water and (iii) water from barometric condensers of evaporators. This disposal contains good quantities of carbohydrates and a low concentration of nitrogen, unlike domestic sewage which has the opposite composition, i.e., low in carbohydrates and rich in nitrogen. This can be released to water bodies without any fear of adverse effects to the ecosystem.
- (b) Wastewater of intermediate concentration: This includes, (i) floor washing, (ii) equipment clean-up water and (iii) sectionizing wastewater. This contains solid waste concentrations ranging from trace amounts to ~2%. This requires some level of treatment prior to disposal to water bodies.
- (c) Concentrated wastewaters: This includes, (i) dripping waters from can closing and filling machines, (ii) effluent from peel-oil centrifugal and (iii) waste alkali from sectionizing or evaporator cleaning. This contains 2–6% of soluble solids and high concentrations of organic materials.

When dilute wastewater is disposed into water bodies, lakes and basins located in far-off places from the residential areas, sandy beds or sandy lands, the liquid in the wastewater can either percolate down into the soil or evaporate easily, leaving behind the solids at the surface. Later, the clogged wastewaters were also suggested for spray irrigation with somewhat diluted concentration to pasture lands [11,12]. One such experiment

conducted at pasture land bearing leguminous cover crops has been reported to show good results [13]. However, spray irrigation to the wood lands, pastures and green vegetation showed negative effects. For disposal, usually, several ponds are constructed, sometimes in series, to manage the waste to flow from one pond to another. The discharge into groves or wells may result in defoliation of trees, probably because of the loss of oxygen in the soil around the roots of the trees. Wastes released into the city sewage system may contaminate the underground water sources and cause damage to pumps and piping, clogging of sand beds and foaming in primary settling tanks. Additionally, pumping the wastewaters into the wells is prohibited because of probable contamination of underground water supplies. Furthermore, fermentation causes gaseous build-up inside the dumping wells and sometimes the pressure mounts to an excessive level to blow back and cause fire outbreaks. Some of the workable solutions in such cases are treatment with nitrogen, extensive aeration and chemical flocculation followed by lagooning [14–17]. Chemical flocculation with lime combined with aeration in order to promote floating of solids has been observed to result in a 64% reduction of suspended solids and up to a 30% reduction in biological oxygen demand (BOD) [18–20]. Although this treatment does not reduce the BOD of the wastewaters, it helps in fulfilling the purpose of waste pre-treatment by regulating the pH to a less acidic consistency and clarifying the suspended solid particles. Common methods of citrus waste removal from the food processing plants and industries, and its adverse effects on the environment, are shown in Figure 1.

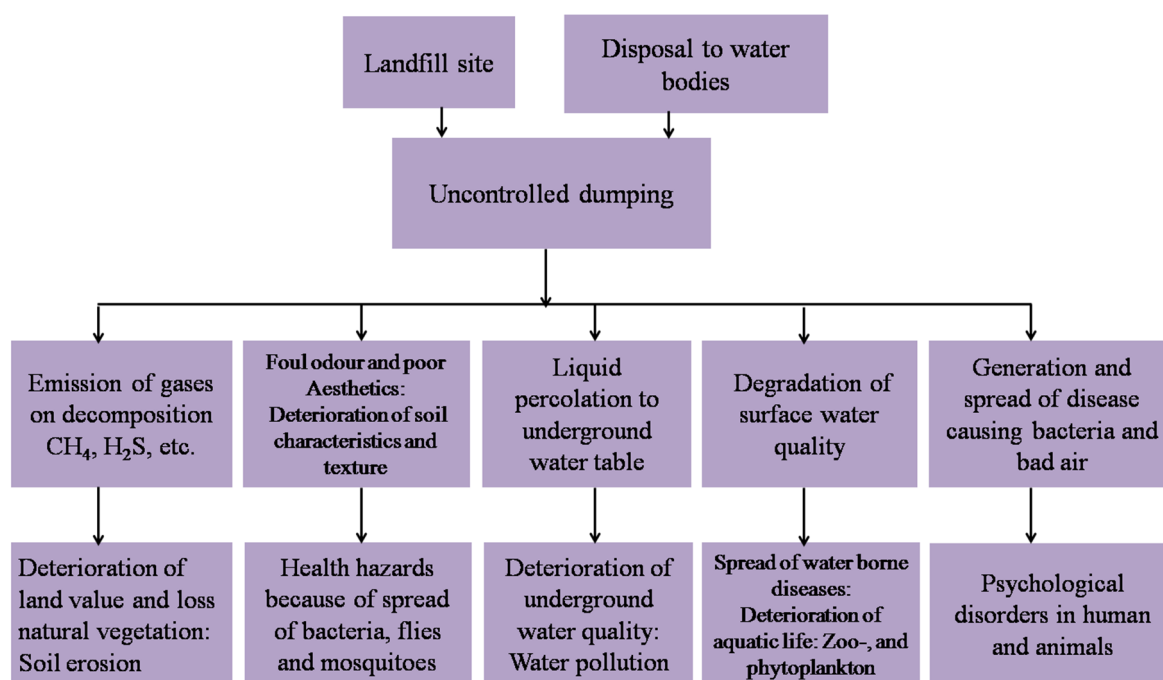


Figure 1. Conventional methods of waste removal from citrus processing plants and deteriorating effects to the environment.

The semi-solid citrus wastes have very high-water content, and they are difficult to dry through conventional methods. Furthermore, these processes consume huge energy. The most common method of solid and semi-solid biowaste management methods is composting. However, in case of citrus waste, it causes additional problems. Composting or digesting the citrus waste is not a practical choice as these contain large amounts of essential oils, mainly limonene, which inhibits microbial growth and the fermentation process and affects decomposition. Therefore, extraction of oils from the peel waste is very important before disposal to the landfills. Murdock and Allen reported that the oils present in the orange peels are toxic to yeasts [19]. These have been found to exhibit inhibitory effects on the growth of several useful bacteria, yeast and molds, e.g., *Bacillus subtilis*,

Saccharomyces cerevisiae and *Aspergillus awamori* [20]. Removal of oils from the citrus waste enables application of decomposition methods or anaerobic digestion, incineration, thermolysis and gasification. Detailed illustrations of practical methods of systematic and environment-friendly disposal of citrus wastes and their relative merits are displayed in Figure 2.

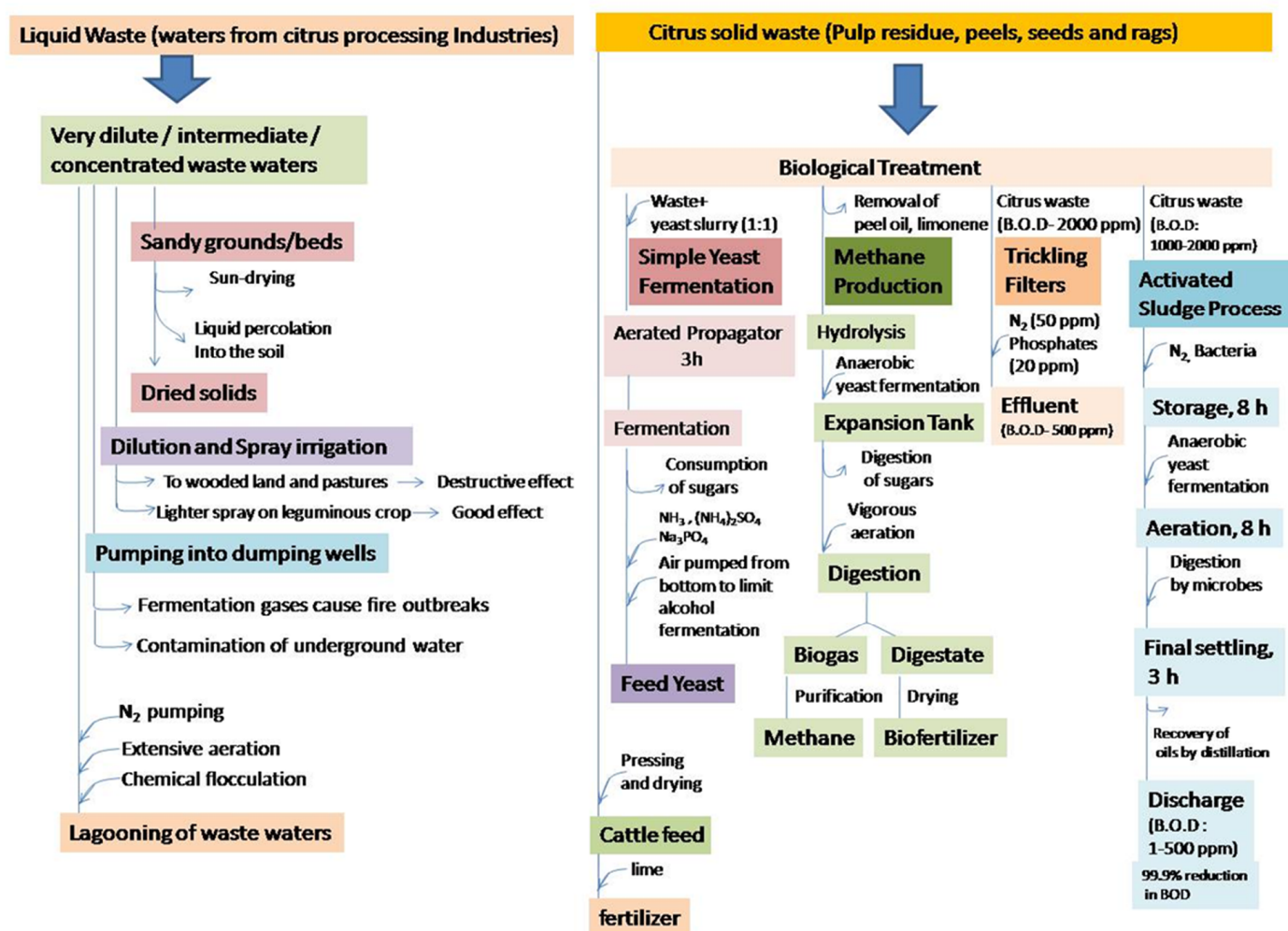


Figure 2. Methods of systematic and environment-friendly disposal of citrus wastes, conversion into useful materials and their relative merits.

Thus, it appears that the extraction of oil from the peel waste streams not only provides useful by-products, but also contributes toward pollution abatement. Citrus wastes also contain large amounts of sugars, which along with moisture, invite bacteria to grow. Decaying waste causes visual displeasure, odoriferous environment and attracts flies. Furthermore, citrus wastes are required to be processed quickly before compositional changes occur. Therefore, waste disposal to the dumping grounds has additional disadvantages. The nitrogen content in the solid waste materials (<0.14%) is quite insufficient to support bacterial decomposition. Therefore, to support decomposition, it robs oxygen from the soil underneath, resulting in a deficiency of nitrogen in the soil. The effect can be witnessed in terms of de-coloration of the vegetation or grasses at or surrounding areas of the dumping ground. The problem can be overcome by adding N₂ supplements in the form of chemical fertilizers. In this process, 200–400 pounds of calcium cyanide is added to each ton of ground waste, mixed thoroughly and allowed to dry until crumbly. Besides calcium cyanides, nitrates, ammonium sulfate and super phosphate are also sometimes added [10].

1.2. Pollutants: Dyes, Heavy Metals, Pharmaceutically Active Compounds (PACs) and Other Contaminants

Processes and manufacturing industries, such as metal plating, metal finishing, automotive, semiconductor manufacturing, pulp and paper production, mining operations, ceramics production, tanneries, radiator manufacturing, smelting and alloy manufacturing, battery manufacturing, corrosion of pipes and infrastructures, textiles and dye industries, etc., release a number of harmful and hazardous chemicals into wastewaters and effluents [21,22]. Researchers have reported that more than 700 kinds of pollutants, both organic and inorganic chemicals, mostly toxic and non-biodegradable in nature, are regularly discarded into the water bodies. The non-biodegradable pollutants are persistent in the environment. The heavy metals in the list of pollutants are cadmium, platinum, mercury, copper, lead, chromium, arsenic, antimony, etc., which have been observed to cause adverse health effects, such as gastrointestinal disorders, stomatitis, tumors, hemoglobinuria, ataxia, paralysis, diarrhea, neurological disorders, muscular dystrophy, vomiting, convulsions and so on [23–25]. Heavy metal pollution is a serious problem because of the metals' persistent nature, and their ability to enter and accumulate in the food chain [26–28].

Dyes are organic compounds used for coloring textile materials, paper, plastic, paints and synthetic coloring materials. There are about 40,000 dyes and pigments with approximately 7000 different kinds of chemical structures known to chemists. A dye substance has two parts: chromophores and auxochromes. The chromophores impart color whereas the auxochromes impart intensity for the dye. The dyes are classified as acid, base, reactive, direct, disperse, solvent, sulfur, vat, etc., and involve a wide variety of applications as well as application methods. A vast majority of dyes and pigments are non-biodegradable and persistent in nature. Textile and fiber industries employ approximately 10,000 different kinds of dyes for dyeing and printing of clothes and fabrics. The concentration of the dye bath during the dyeing processes ranges between 10 and 200 mg L⁻¹, which retains approximately 10–15% of its initial concentration post-dyeing and released into the effluent [29,30]. The dye concentration of approximately one ppm or less in the wastewaters has been considered as a potential threat to the environment and to human and aquatic lives [29]. Cyanides from industries released into the environment, particularly in wastewaters, have detrimental effects. Cyanides and their complexes have been demonstrated to have bio-accumulative properties that result in ecological deterioration [31]. Most of the industrial wastewaters contain F-CN, the simplest and most toxic form of cyanide, which is formed by dissociation of cyanide complexes during cyanide-based electroplating operations [32]. Chemical methods are usually employed for the conversion of free cyanide (F-CN) into a complex of NH⁴⁺ and CHOO⁻, but most of the methods are expensive. Furthermore, they also produce harmful by-products which contribute to environmental contamination as well as being detrimental to the bioremediation processes [33]. Citrus wastes have been found to be useful for the conversion of F-CN into a complex of NH⁴⁺ and CHOO⁻. Apart from F-CN, most of the wastewaters contain heavy metals and the presence of the metallic species (Ni, Zn, As, Cr, Hg and Cu), which have been observed to slow down the conversion of F-CN. The latter occurs as the metallic ions become attached to the hydroxyl groups of the absorbent material responsible for the removal. In addition, it has been reported that material obtained after acid hydrolysis of citrus solid wastes increases the catalytic conversion of F-CN by ~3.86-fold compared with the unhydrolyzed solid waste. The conversion has been found to increase linearly with an increase in pH and temperature [33]. Adsorption of heavy metal ions on the adsorbate material is fundamentally driven by electrostatic attraction between the oppositely charged ions. Both the heavy metal ions present in the wastewater and the functional groups (-COOH, -OH) present on the bio-sorbent material carry charges. The electrostatic attraction between the charges results in binding and ion exchange between Na⁺, Mg²⁺, K⁺, Ca²⁺ and heavy metal ions (M²⁺). However, the ion exchange predominates due to stronger binding forces between the charged species.

In recent years, pharmaceutically active compounds (PACs) are emerging as one of the most harmful contaminants in the natural and wastewater systems. PACs are the vast range of complex organic chemical formulations which possess a range of medicinal properties and are used in the treatment, control and eradication of diseases in both humans and animals. These include antibiotics, anti-inflammatories, cytotoxins, birth control pills, synthetic hormones and statins. The commonly encountered PACs in surface waters are erythromycin, metronidazole, sulfamethoxazole, trimethoprim, ciprofloxacin, amoxicillin, trimethoprim, tetracyclin, metformin, acetaminophen, diclofenac, ibuprofen, ketoprofen, naproxen, diazepam, fluoxetine and so on [34–37]. In the past few decades, consumption of pharmaceutical compounds has increased compared with many earlier decades in the century across the globe, resulting in a significant increase in the production of raw materials as well as the final PAC products. Manufacturing of PACs and life-saving drugs by the pharmaceutical companies and processing and packaging factories also releases huge amounts of compounds into the wastewaters. When excreted by humans or animals and disposed of inappropriately, these enter into the environment. In addition, PACs are also released by urban sewage, domestic hospital wastewaters, intensive livestock farming, liquid livestock manure production, sewage sludge from agricultural activities and effluents from sewage treatment plants [38]. The compounds undergo transformation into certain metabolites or breakdown compounds under the influence of temperature, light and vicinity of other chemical ingredients or microbes in nature under the process of biodegradation or photodegradation. Hence, the new molecules produced may sometimes be more toxic compared to their parent PACs. Furthermore, the transformation renders it difficult to monitor the presence of PACs in their original parent formulation in the environment (ground or surface waters). Presence of PACs in significant amounts in the drinking water has become an alarming concern in many countries. These compounds are capable of accumulating in the biological entities, primarily microbes, and making them drug-resistant. As a consequence, they lose their potency to act effectively against disease-causing microorganisms. Apart from drug resistance developments in disease-causing pathogens, PACs in the environment also cause feminization of male fish and amphibian species because of enhanced amounts of natural and synthetic estrogens in the habitat waters. In addition, increased amounts of PACs in irrigation waters to the crops produce food enriched with PACs. Such foods have been found to cause femaleness in human males, multiple organ complications/failure, genetic and hereditary diseases [38,39].

Diclofenac, a non-steroidal anti-inflammatory (NSAID) drug, has been extensively employed in veterinary usage, fever, pain and injury, livestock farming, fisheries and dairy industries, and has resulted in increased amounts of this chemical in the flesh of animals. When the animals die and are fed upon by predatory birds, diclofenac enters into their bodies and causes serious health consequences, leading to death and collapse of their population. Genus *Gyps*. is most severely affected and has been included in the category of global extinction risk. Some of the highly endangered species from genus *Gyps*. are oriental white-backed vulture (*Gyps bengalensis*), long-billed vulture (*Gyps indicus*) and slender-billed vulture (*Gyps tenuirostris*), and the decline in their population has been recorded to be more than 95% since the early 1990s. The decline has been observed to continue at an annual rate of 22% to 48% [40–43]. Diclofenac causes kidney damage, increases in the concentration of uric acid and crystal formation in serum and vital tissues, visceral gout, bone tumor and death of the predatory birds. Decline of predatory birds' populations in the ecosystem has been reported to cause a severe imbalance in the food chain and an alarming threat to the survival of the human population in Europe and Asia. Absence of the predatory bird population (eagles and vultures), or scavengers of wild and domestic ungulate carcasses in the ecosystem, has led to an increase in the population of feral dogs (*Canis familiaris*), and consequently, an increased risk of rabies spread in the human population. Furthermore, there has also been an alarming increase in the population of rats (*Ratus* spp.) and increasing risk of transmission of various diseases observed, such as bubonic plague, brucellosis, tuberculosis and anthrax in humans and

livestock. Disappearing eagle and vulture populations have also created a huge challenge for the Parsee and Tibetese communities in India, Nepal and Tibet, as they find it difficult to continue their burial ritual/practices at sky burial sites and towers of silence [39].

1.3. Health Hazards of Pollutants

Metal industries related to mechanical works and battery manufacturing carrying out electroplating, metal plating, etc., release substantial amounts of heavy metals into the wastewaters. Additionally, large amounts of poisonous dyes are released from pigments or printing industries [44]. The pigment and dye industries produce different kinds of dyes, such as methylene blue (MB), oxazine and xanthenes compounds, azo dyes, methyl violet, etc. Among various dyes, methylene blue and heavy metal salts are the most frequently used chemicals for dyeing silk, wood and cotton [45]. MB is a common cationic dye extensively used in medical, textile and printing industries. The wastewater effluents from these industries contain high amounts of dyes, which can cause severe environmental pollution. It contaminates the water bodies, such as rivers, ponds, lakes, ditches and even the ground waters. These chemicals are toxic and cause severe impacts on human health as they may cause nausea, vomiting, diarrhea, etc., when ingested. Thus, removal of MB from wastewater is of great concern not only from an environmental point of view, but also for the sake of human life. Various methods used for dye removal include adsorption, flocculation, precipitation, ion exchange, electro-kinetic coagulation, ozonization and so on. Among the above-mentioned processes, adsorption is one of the most efficient methods due to its simple design, ease of operation and insensitivity to toxic substances [46]. The molecular structures of some of the popular anionic and cationic dyes are shown in Figure 3. The hazardous effects of dyes and heavy metals on human health, the ecosystem and the environment, and the possible use of citrus waste-derived bio-sorbents for the removal of harmful chemicals from the wastewaters, are illustrated in Figure 4. The permissible limits and the hazardous effects of heavy metals, dyes and other contaminants on human health have been summarized in Table 1.

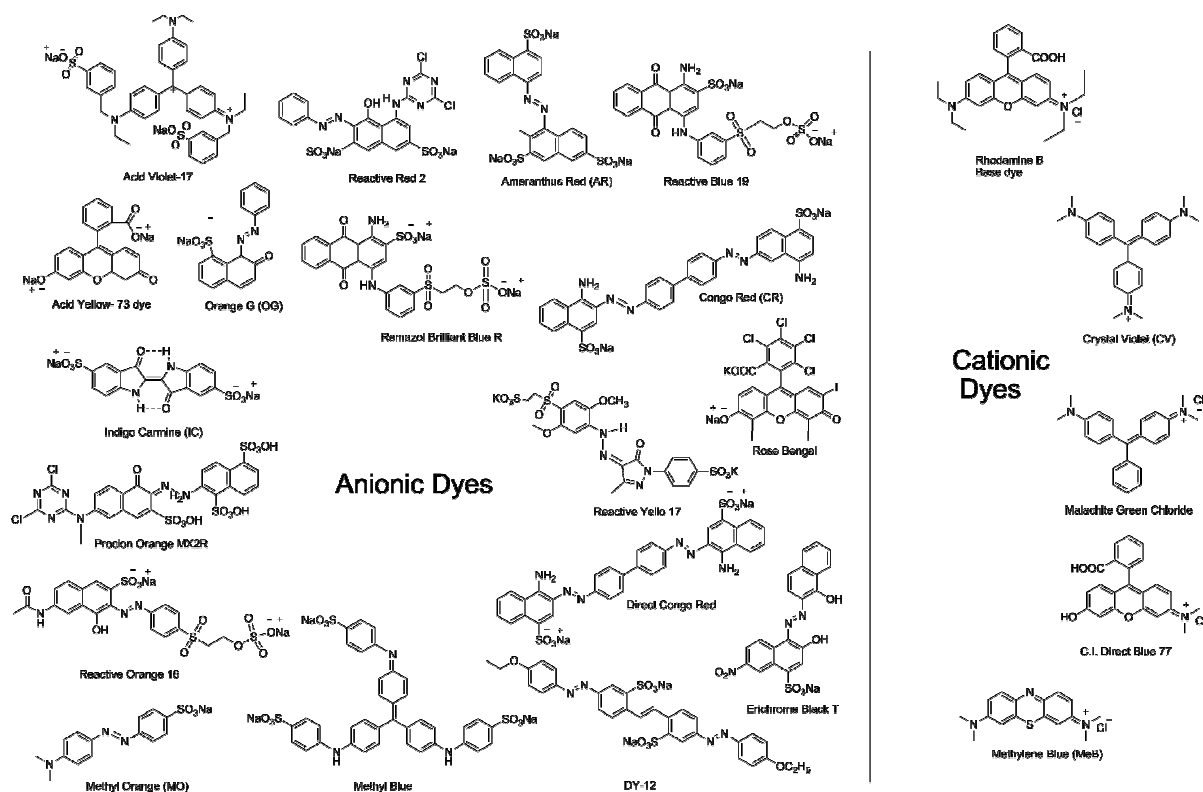


Figure 3. Structures of the anionic and cationic dyes.

Table 1. The permissible limits and the hazardous effects of heavy metals, dyes and other contaminants on human health.

Heavy Metals	Allowed Limits (WHO/EPA); mgL ⁻¹	Source of Contamination	Adverse Effects on Health	Ref.
Arsenic	0.01	Erosion of natural deposits, runoff from soil in orchards, glass and electronics manufacturing waste, tanneries	Skin damage, deformation of digits, cancer, deterioration of circulatory system	[48]
Beryllium	0.004	Metal refineries, coal burning, discharge from electrical, aerospace and metal finishing factories/industries	Gastrointestinal disorders	[49]
Cadmium	0.005	Corrosion of pipes and infrastructures, erosion of metal in refineries, battery waste, paints and dyes	Kidney damage, cancer of lungs, malfunctioning of vital organs, proteinuria	[50]
Chromium	0.05–0.25	Steel industries, metal finishing factories, pulp mills and corrosion of stainless steel pipes and infrastructures, tanneries	Allergy, dermatitis, hemolysis, kidney failure, carcinomas, mutagenic diseases	[51]
Copper	1.0–1.3	Corrosion of household utensils and artefacts, plumbing system, erosion from copper mines	Gastrointestinal disorders, abdominal irritation, liver and kidney damage	[52]
Lead	0.005–0.015	Battery waste, corrosion of pipes and plumbing system, solder joints, erosion from natural deposits	Retardation of growth in children, abnormality in mental health and physical growth, anemia, vomiting, kidney and liver damage, high blood pressure	[49,53]
Mercury	0.002	Erosion from natural deposits, discharge from refineries and factories, runoff from landfills, croplands	Hypersensitivity, fever, vomiting, neurological disorders	[49]
Selenium	0.01–0.05	Petroleum refineries, erosion from natural deposits and mining sites	Loss of hair and finger nails, red skin, numbness in fingers and toes, burns, circulatory system disorders	[49]
Zinc	5	Electroplating industry, galvanization of metals, motor oil, battery waste, hydraulic fluid, tire dust	Corrosive to skin and eyes, zinc pox, sweet taste, throat dryness, cough, weakness, generalized aching, chills, fever, nausea, vomiting	[54]
Dyes	Less than 1.0 ppm	Effluents from fiber and textile industries, paper and pulp industries, plastic industries, paint industries	Nausea, vomiting, diarrhea	
Fluoride	1.5	Fluoride deposits (rocks such as topaz, cryolite and fluorapatite, etc.) on earth. Electroplating, glass, ceramics, steel manufacturing and phosphate fertilizer production; semiconductor manufacturing factories, pharmaceutical companies, beryllium extraction plants, aluminum smelters, fertilizer manufacturing and mining industries	Dental and skeletal fluorosis, crippling	[55,56]
PACs (Pharmaceutically active compounds)	50 ngL ⁻¹ to 0.1 µgL ⁻¹	Pharmaceutical manufacturing plants, urban sewage, domestic hospital wastewaters, intensive livestock farming, liquid livestock manure production, sewage sludge from agricultural activities and effluents from sewage treatment plants	Genotoxicity and carcinogenicity, multiple drug resistance in pathogenic microorganisms, femaleness in males, tumor and vital organ failure in predatory birds	[49]

1.4. Citrus Peel-Derived Adsorbent Materials

The most popular adsorbent for the adsorption process is activated carbon. However, its use is still limited because it is expensive in terms of its high operational cost [57–59]. Advanced technology enables scientists to attempt to overcome the cost of the treatment process by using inexpensive, efficient and easily available adsorbents. In the literature, numerous studies have been reported to obtain low-cost activated carbons from agricultural wastes, such as wheat shells, rice husk, tea waste, neem leaf powder, cotton waste, banana peel and orange peel for the removal of heavy metals and other hazardous compounds from wastewaters [60–65]. However, the sorption potential of most of these low-cost sorbents is limited. The surface of the bio-sorbent can be modified to enhance its activity. Among many low-cost adsorbents, one such inexpensive and economical adsorbent precursor material is citrus fruit peel [66,67]. Citrus fruit peel has no use after the extraction of essential

oils and other valuable chemicals, and thus, it is a commercially valuable and readily available resource for making adsorbent materials. Hence, conversion of citrus fruit peel to low-cost adsorbents serves multiple purposes. The unwanted waste can be converted to value-added products, such as low-cost adsorbent materials for the removal of heavy metals and dyes from aqueous solution. The latter efficiently alleviates the environmental pollution. Types of modification that can be introduced to the biomass-derived bio-sorbents are shown in Figure 5.

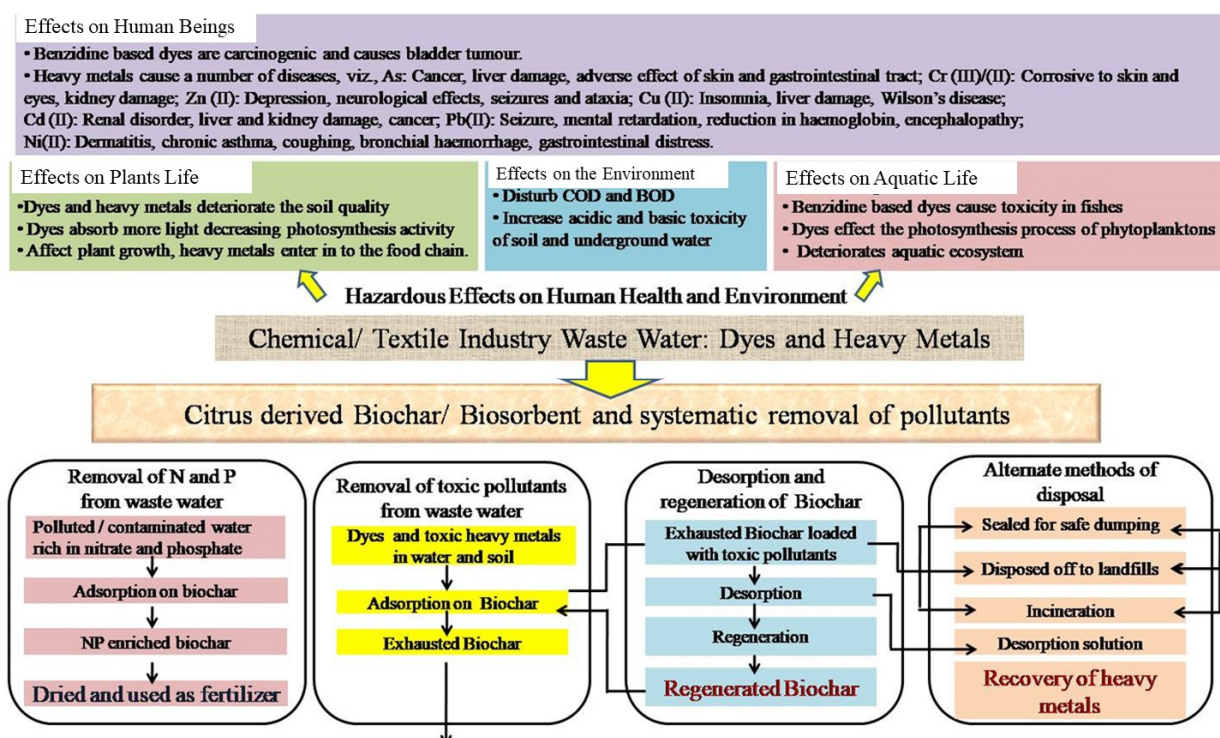


Figure 4. Hazardous effects of dyes and heavy metals released in the effluents from chemical and textile industries on humans and the environment, and the possible use of citrus waste-derived bio-sorbents for the removal of harmful chemicals from the wastewaters. Artwork developed from the information provided in [47].

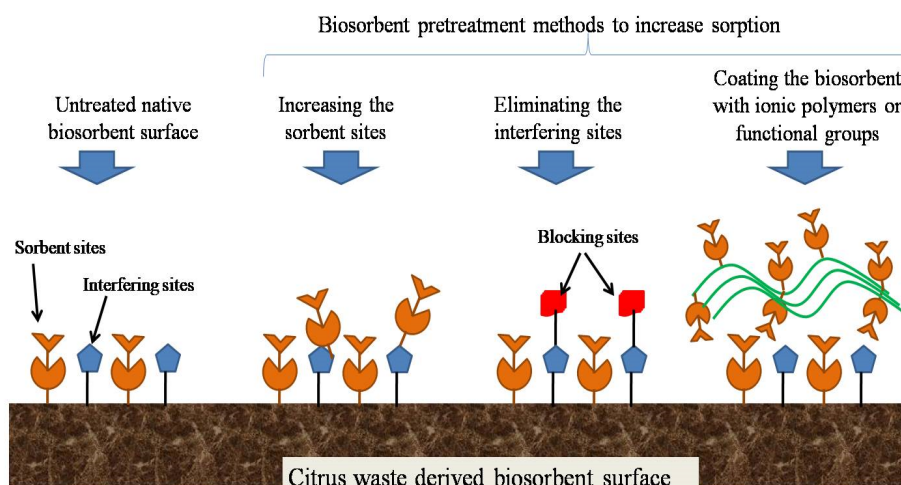


Figure 5. Basic principle of surface modification of citrus waste-derived bio-sorbent material by chemical pre-treatment for the removal and recovery of heavy/precious metals. Artwork created from the information provided in [68].

In this article, we focus on reviewing the recent progress in the field of citrus biomass research focused on producing energy, biofuels, important chemicals and bio-sorbent materials for the adsorption of dyes, heavy metals and toxic chemicals by processing of citrus waste biomass via biotransformation. Biotransformation is the modification of waste biomass or harmful chemical substances by certain microorganisms or chemical agents to render them either harmless to humans and the environment or for synthesis of useful products for safe consumption. The review has been presented in two parts under the titles “*Biotransformation of Citrus Waste-I: Production of Biofuel and Valuable Compounds by Fermentation*”, and “*Biotransformation of Citrus Waste-II: Bio-sorbent Materials for the Removal of Dyes, Heavy Metals and Toxic Chemicals from Polluted Water*”. The first part deals with the synthesis and production of biofuels (ethanol, methane and biodiesel) and valuable compounds, such as organic acids (citric, succinic, pyruvic, lactic, acetic), Vit-C, enzymes, single-cell proteins and prebiotics from fermentation of the citrus wastes [8]. In the second part of the article (present article), we attempt to review current and conventional trends of citrus waste disposal and their relative merits, and recent progress in biotransformation of citrus waste biomass into bio-sorbent material, employing physical, chemical or thermochemical methods for the adsorption of various pollutants, mainly heavy metals and dyes from polluted wastewaters and industrial effluents, and mechanisms and theoretical studies explored in the adsorption processes. The motivation behind this review is to conduct a detailed overview of the recent updates in this area of research and emphasize our focus towards the possibilities of harnessing the hidden potential of obtaining efficient products out of citrus biowaste, which otherwise is discarded in the dumping grounds as waste.

2. Methods of Preparation of Bio-Sorbents

Bio-sorbents from citrus wastes have been developed in a number of ways, such as (a) mechanical shredding/grinding, (b) physicochemical treatment, (c) thermochemical treatment and (d) biochemical methods using enzymes. Based upon the treatment, the different kinds of bio-sorbents obtained from citrus waste can be classified into the following categories: (i) native peel bio-sorbent, (ii) protonated peel bio-sorbent, (iii) peel pectic acid bio-sorbent, (iv) de-pectinated peel bio-sorbent, (v) carbonized peel-activated carbon bio-sorbent, (vi) chemically modified bio-sorbent and (vii) biochemically or enzymatically modified bio-sorbent. The native peel bio-sorbents are obtained from physical or mechanical treatment of citrus peel biowaste. The biomass is washed with tap water to remove dirt, followed by washing with distilled or deionized (DI) water, or nano-pure (NP) water, 3–5 times. Washing is a common step and is essentially included in all the techniques of biomaterial preparation. The native peel bio-sorbent is developed from drying the washed peel waste at 323 K, until it attains a constant weight, followed by grinding and sieving to a desired particle size of ~0.5–1.0 mm, appropriate for adsorption studies. Peel pectic acid is prepared from albedo of the citrus peel waste. The peels are treated with hot acidified water (HCl, pH 1.5) at 358 K and stirred for 2 h. The treatment at elevated temperature facilitates extraction of pectic acid from the peel tissues. The extracted pectic acid is then filtered and coagulated with an equal volume of ethanol (95%). The coagulate is washed with ethanol and dried until constant weight. The peel pectic acid is insoluble in aqueous medium and remains stable during the adsorption tests [40]. The de-pectinated peel adsorbents are obtained from the residue remaining after the extraction of pectin from peel waste. The pectin is mainly extracted from the albedo (white) part of the peels. The residue is washed thoroughly and dried in an oven until constant weight [1,2].

Chemical modification of bio-sorbents is carried out in order to enhance the adsorption capacity by introducing active functional groups by means of chemical reactions. Furthermore, it helps in enhancing the chemical stability and mechanical properties of the sorbent material. The latter prohibits the release of pollutants into the adsorption system. Chemical treatment is carried out via several methods. Some of the well-known methods are: (a) protonation (inorganic acid: HCl, H₂SO₄, HNO₃), (b) alkali saponification (using NaOH, Ca(OH)₂, CaCl₂), (c) phosphorylation, (d) blocking of functional groups

using chemical reagents, (e) organic acids (citric acid, oxalic acid), (f) H_2O_2 treatment, etc. Protonated peel bio-sorbents are obtained from protonation of the citrus peel waste collected after washing and drying. The protonation is carried out by treating the material with acids, such as HCl or HNO_3 . For this, the material is suspended in the acid and stirred or shaken for 6–8 h, followed by filtration, washing until neutral pH and drying until constant weight. Protonation is employed to remove excess of cations, such as Ca^{2+} or Na^+ , present on the biomaterial surface, which interfere with the metal sorption process. These cations are replaced by protons, which enhances the binding of heavy metals by decreasing the competition between Na^+ , K^+ and Ca^{2+} ions with heavy metals such as Cd^{2+} , Hg^{2+} , Pb^{2+} , Zn^{2+} , Se^{2+} , As^{2+} and so on. Replacement of Ca^{2+} and Na^+ ions by protons has exhibited enhancements in the adsorption of desired heavy metal ions and their removal from wastewater. Treatment with NaOH and citric acid is employed to introduce carboxyl groups on the bio-sorbent surface, which interact with heavy metals to form a complex, and the resultant structure helps in the removal of the toxic elements from the wastewater. Phosphorylation is employed to introduce abundant alcoholic “-OH” groups and phosphoric groups into the bio-sorbent material. The latter, possessing a high affinity for ferric iron, enhances the loading capacity for iron. Iqbal et al. carried out experiments to block “-COOH” and “-OH” functional groups using anhydrous CH_3OH , and concentrated HCl and HCHO , respectively. The modified bio-sorbents with blocked functional groups were found to exhibit a reduced adsorption capacity of Ni^{2+} by 78.57% and Zn^{2+} by 73.31%, confirming the main contribution of carboxyl and hydroxyl functional groups in the adsorption of heavy metal ions [69].

In the carbonization process, the dried peels are subjected to a very high temperature of ~ 773 K, followed by acid oxidation. An inert atmosphere, such as N_2 , is employed to prohibit fire or rigorous oxidation. The positively charged amine groups present on the surface of the adsorbent material facilitate binding to anionic RMB reactive dye by electrostatic attraction [70]. Bhatnagar et al. prepared a bio-sorbent from lemon peels by thermal activation at 323 K in the presence of air, which converted the peels to ash. Treating bio-sorbents with H_2O_2 has been employed to avoid the release of color in bio-sorbents [71]. Treating with 1% NaOH and ethanol removes lignin and colored pigments. Carbonization through the chemical activation method is one of the most favored methods for preparation of adsorbent material from citrus fruit peel. Weight ratios of peel vs. activating agent, temperature and time of carbonization are the selected parameters for optimizing the preparation of an efficient adsorbent material [72]. Generally, the dried citrus fruit peel is fed to a mixer grinder, and the ground powder is mixed with activating agents such as ortho-phosphoric acid, zinc chloride or sulfuric acid. This is then carbonized in a muffle furnace by heating it at an elevated temperature of ~ 723 – 823 K, up to a duration of 0.75 to 1.5 h. The weight ratio of dried citrus fruit peel to activating agent varies in the range of 1:1 to 3:1. The charred material is then cooled and washed with dilute ammonia solution and distilled water. This removes any unconverted activating agent from the carbonaceous material. The washing of the sample 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 [72].

Cross-linked hydrogel adsorbents for the removal of dye molecules can be prepared by treating the ground peel powder with N-vinyl-2 pyrrolidone (NVP), followed by irradiation with gamma rays. Mahmoud et al. demonstrated that a gamma irradiation dose of 30 kGy to the hydrogel precursor composition of NVP and orange peels in the ratio of 1:1 results in optional homogeneity of the bio-sorbent material with appropriate properties for practical applications. Usage of hydrogel (cross-linked polymerized hydrogel) enables the material to adsorb and retain large volumes of water and facilitate in increasing the contact time between the pollutant dyes and adsorbent material by the virtue of its cross-linked three-dimensional network structure. A porous material possesses additional benefits in terms of extended surface area for adsorption [73]. Chemical treatment by formaldehyde and urea carried out by Rabia et al. demonstrated an enhancement in roughness and unevenness,

with apparent pores and canals of irregular shapes in a 3D network structure of the material surface to facilitate extended contact time between the adsorbate molecules and adsorbent material, and enhance physisorption [74]. Treating with HCHO improves the shelf-life of the bio-sorbent and prevents microbial damage [75]. While the functional groups, such as carboxylic acid, amine and sulfonic acid groups participate in electrostatic interaction and binding with dye molecules, the bulky structure of the hydrogel can be conveniently collected, separated and regenerated either by washing with water or treating with acid for further usage. Dev et al. reported on the adsorption of selenium from wastewater by citrus peel-based bio-sorbents chemically modified by calcium alginate. The chemical modification provides structural stability to the adsorbent material, which allows its reusability. Besides, it enhances the number of “-COOH” and “-OH” functional groups due to alginate beads, which enables the bio-sorbent material to absorb and remove other metallic ions in addition to SeO_4^{2-} and SeO_3^{2-} [76].

Kam and Lee carried out adsorption of amoxicillin onto the activated carbon surface prepared from citrus peel waste from aqueous solution containing the antibiotic, and reported an efficient adsorption within 30 min and attainment of equilibrium in 90 min. The waste citrus peel-based activated carbon showed a maximum adsorption capacity of 125 mg/g of the adsorbent at 293 K [77]. Putra et al. studied adsorption and removal of amoxicillin using commercial activated carbon [78]. Moussavi et al. reported on the adsorption studies of amoxicillin on commercial activated carbon and activated carbon derived from pomegranate wood [79]. Ding et al. developed activated carbon from sewage sludge and oil sludge and reported adsorption and removal of oxytetracycline and chlortetracycline [80]. Baccar et al. obtained activated carbon from olive-waste cake to absorb naproxen, ketoprofen, diclofenac and ibuprofen from aqueous solution containing the contaminants [81]. Ahmed et al. produced activated carbon from Siris seed pods and carried out adsorption and removal of metronidazole from contaminated water [82]. On the other hand, activated carbon developed from vine wood by Pouretedal and Sedech et al. showed efficient adsorption of amoxicillin, cephalexin, tetracycline and penicillin from contaminated water [83].

The adsorption of heavy metal ions onto the adsorbent surface is influenced by several factors, such as nature of the material, charge on the chelating metal ion, size of the ion, nature of donor atom present in the ligand, buffering environment during the adsorption process and exchange of ions, nature and properties of the solid support, and so on [84]. In this direction, Li et al. carried out chemical modification employing 20% isopropyl alcohol to remove coloring compounds from orange peels, along with polar compounds. This was followed by saponification by addition of 0.1 M NaOH/0.1 M NH_4OH /saturated solution of $\text{Ca}(\text{OH})_2$. The $\text{Na}^+/\text{NH}_4^+$ or Ca^{2+} ions become attached to the cellulose molecules of the adsorbent material and facilitate an ion exchange mechanism between Na^+ , NH_4^+ or Ca^{2+} ions and the bivalent heavy metal ions. In the next step, the saponified orange peels are treated with 0.6 M acid at an elevated temperature of 353 K. The heat is required to produce a condensation product and acid anhydride. The latter combines with cellulose hydroxyl groups and results in the formation of ester linkage and introduction of carbonyl groups to the cellulose molecule. The additional carbonyl functional groups introduced to the cellulose molecule enhance metal ion adsorption [85]. In another method, Liang et al. treated orange peels with NaOH followed by mercaptoacetic acid ($\text{C}_2\text{H}_4\text{O}_2\text{S}$) in order to convert the hydroxyl groups present in the cellulose molecules into mercapto groups. The latter exhibited a higher affinity towards heavy metal adsorption (Cu^{2+} and Cd^{2+}) from aqueous solutions [86]. The final different sized samples are used for adsorption purposes. The different methods of bio-sorbent pre-treatment by heat, chemical(s) and enzymes are summarized in Figure 6.

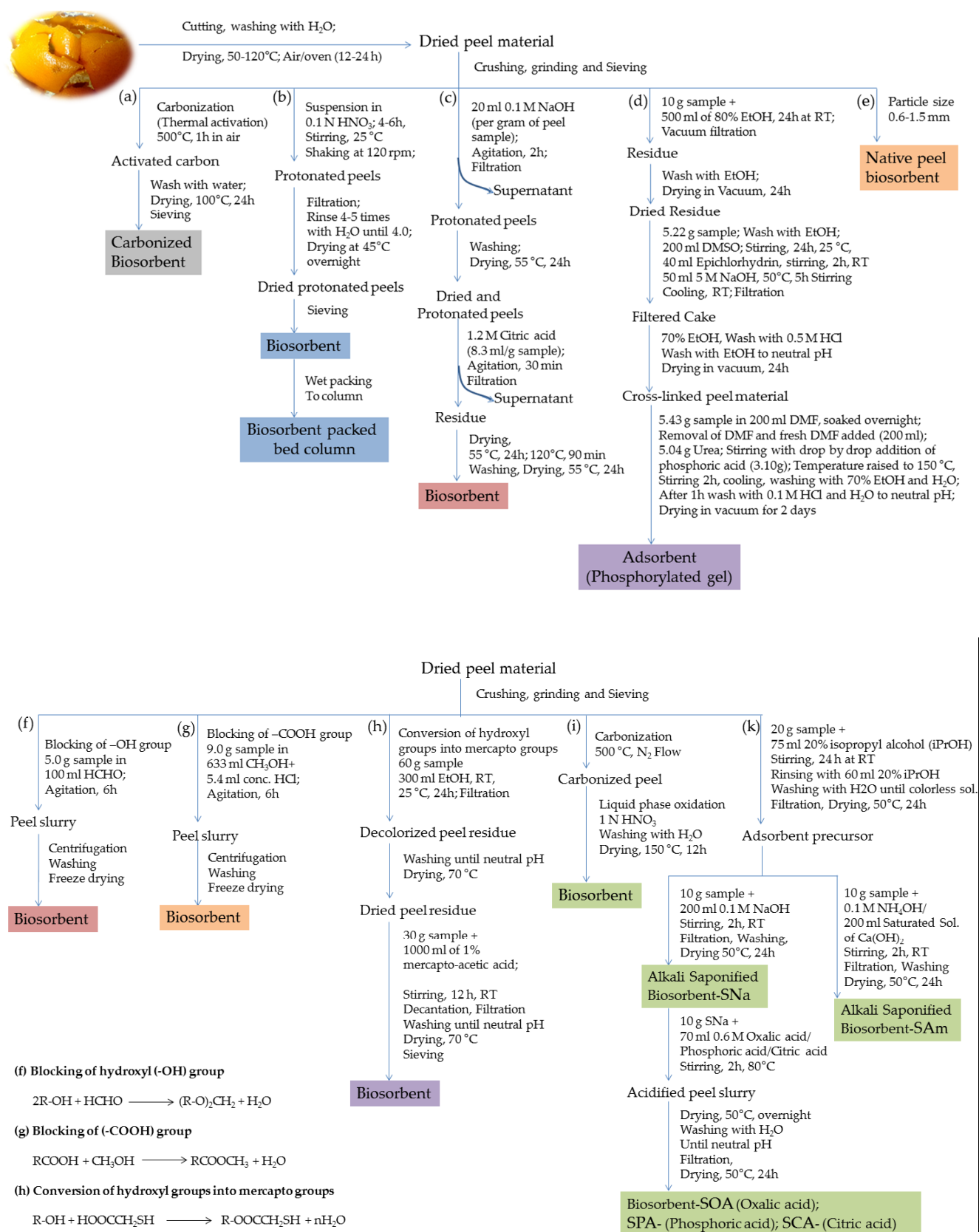
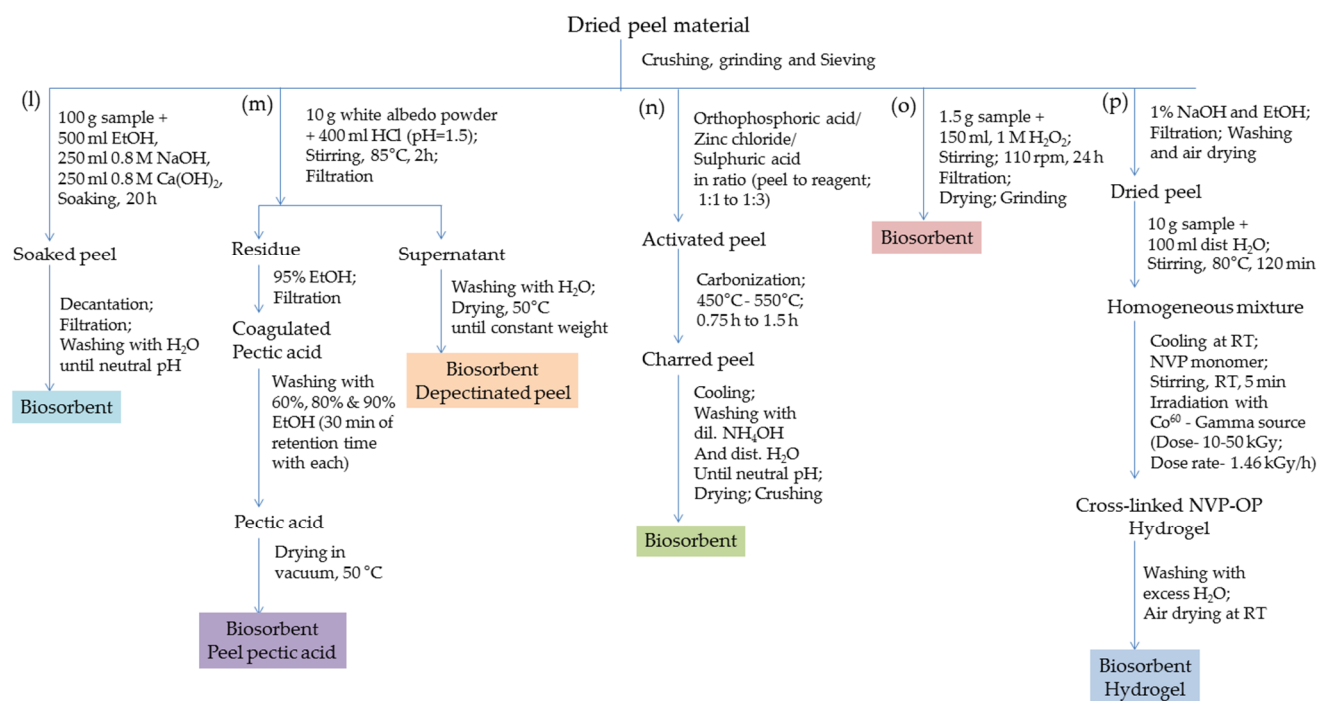


Figure 6. Cont.



NVP - N-vinyl-2-pyrrolidone

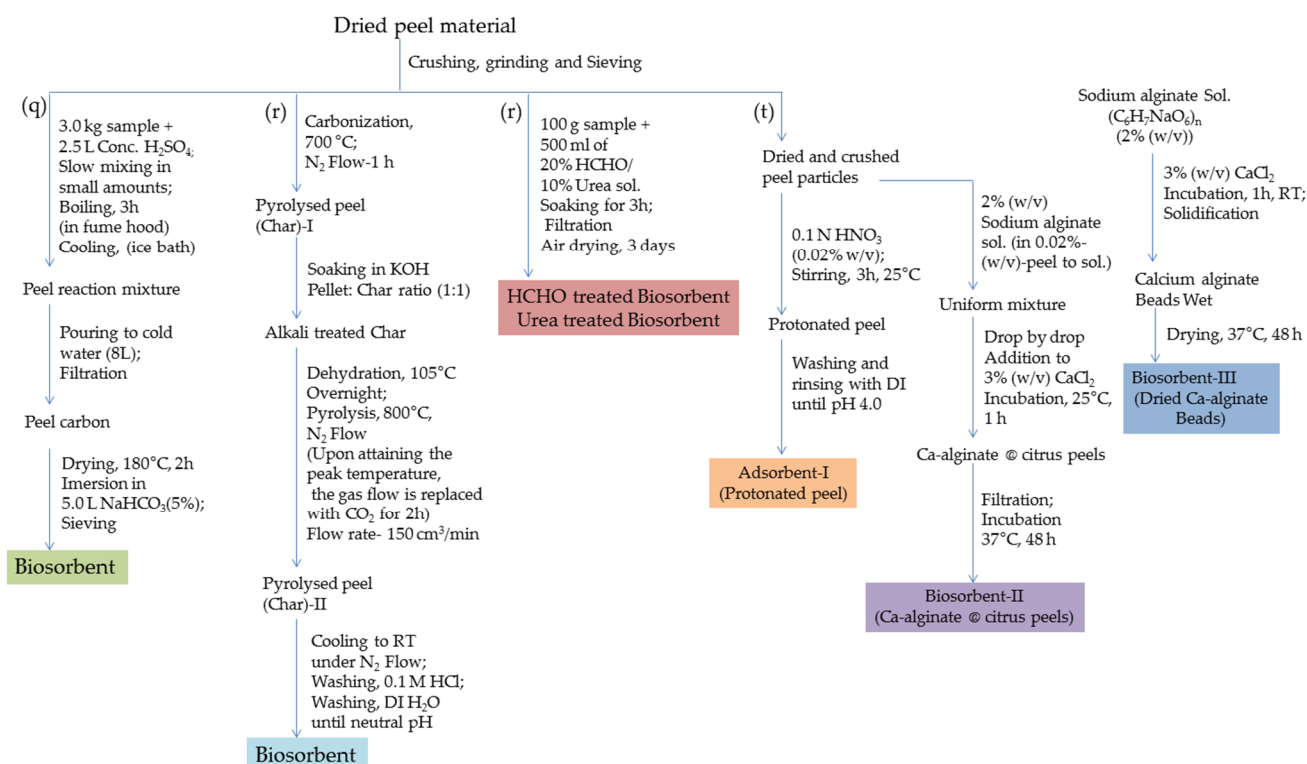
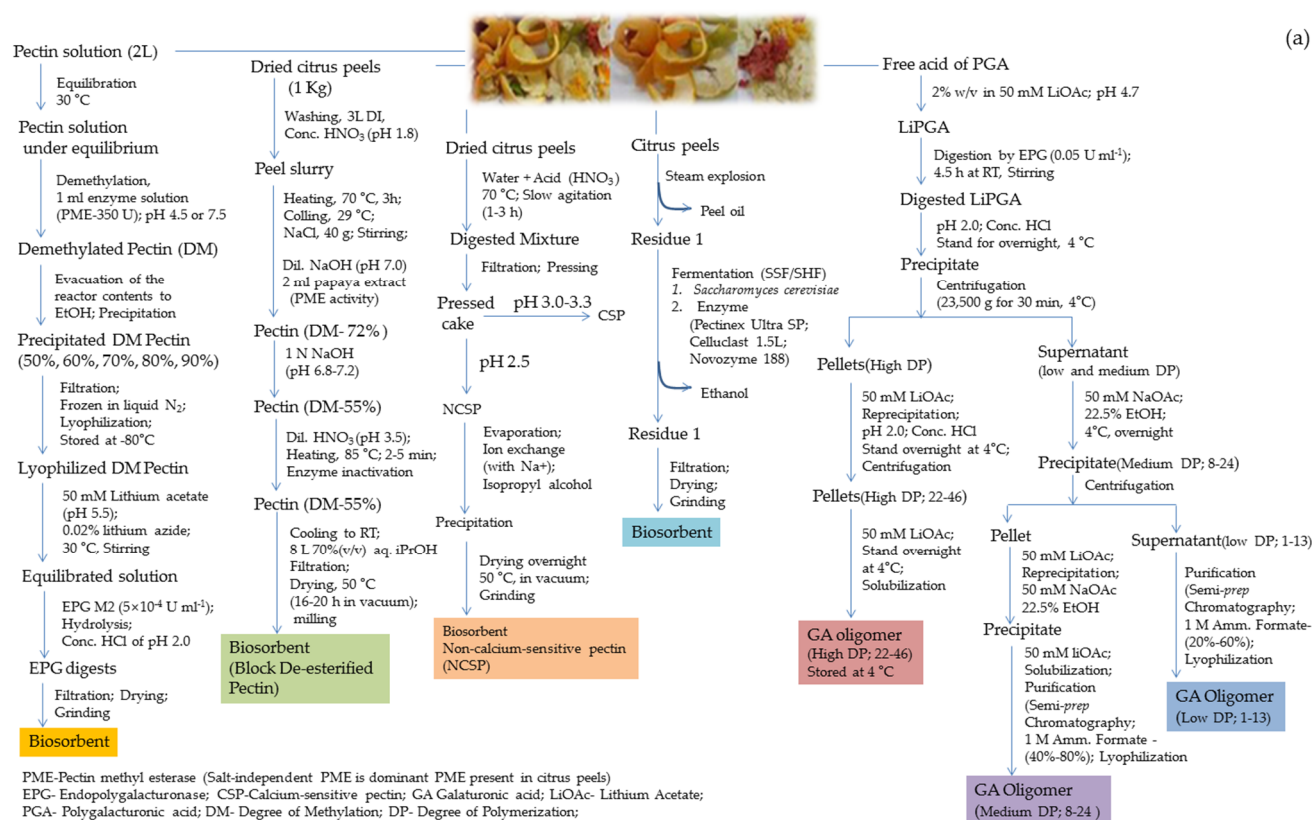
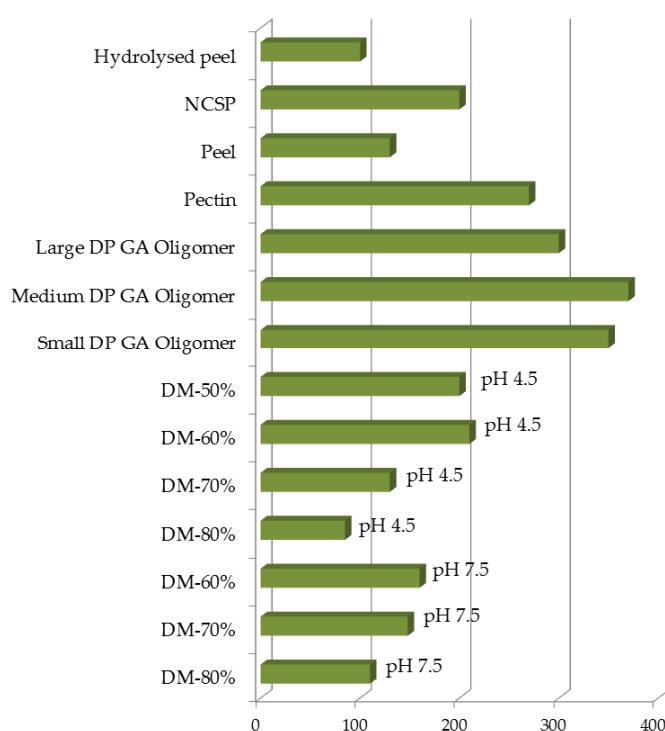


Figure 6. (a–t) Different methods of pre-treatment of the precursor material for the preparation of bio-sorbents from citrus wastes [69–76,84–88].

Cameron et al. carried out an elaborated study on the adsorption of Pb^{2+} ions by adsorbents synthesized from citrus peels and peel-derived pectin and concluded that fragmentation of larger molecules into smaller fragments and demethylation of the same occur. The latter plays an important role in the enhancement of the sorption capacity of pectin and derived materials. The fragmentation can be carried out either chemically or enzymatically. Pectin, a polysaccharide present in the citrus peels, can be modified via enzymatic or chemical conversion to develop a suitable bio-sorbent as well as fine-tune the desired properties, e.g., ion exchange and adsorption properties. Pectin polymer is made of galacturonic acid (GA) monomer units, a major sugar found in citrus fruits. It is basically concentrated in the linear homogalacturonan region (HG), which is pectin's dominant structural domain. The carboxylic acid functional groups present in the GA molecular structure interact with the heavy metal cation present in the wastewater or industrial effluents and require removal. While the polyanionic character of pectin is crucial for adsorption, masking of the negative charge present on the carbonyl group in the GA molecule by means of methyl esterification at C-6 position hence alters the overall functionality of the pectin molecule. In other words, the pectin functionality is dependent upon the total amount of methylation of GA units or degree of methylation (DM) and distribution of methylated GAs and non-methylated GAs (GAs with unmasked or free carboxylic acid functional groups) in the pectin polymeric chain in the HG region [89]. The de-esterification of the GAs or de-methylation of GAs can induce ordered or random distribution of de-methylated GAs in the pectin polymer chain. Both kinds of specific properties obtained post-modification, e.g., degree of methylation (DM) and degree of polymerization (DP), in pectin molecule have been reported to exhibit effects in terms of interaction with cation and sorption properties [87,88]. Pectin extraction can be carried out via aqueous extraction using an aqueous acid or base followed by purification of liquid extracts containing hydrocolloids, and isolating the extracted pectin from the mixture [1,2]. There is a basic difference in the product quality of pectin obtained post-acid/alkali treatment. The pectin obtained from the alkali extraction process contains a low degree of esterification (low DE pectin). The latter results from saponification of the ester groups present in the polymer molecule by alkali. On the other hand, pectin obtained from the acid extraction process contains a high degree of esterification (with high DE pectin ~50% and greater) [89]. The methods of obtaining bio-sorbent materials from citrus peel-derived oligosaccharides and enzymatically modified pectin have been summarized in Figure 7a, and their respective adsorption capacities towards Pb^{2+} are shown in Figure 7b.



Biosorbent Substrate

mg Pb · g Sample⁻¹

- NCSP- Non-Calcium Sensitive Pectin
- Hydrolysed peel- Lyophilized material from a single state fermentation of citrus peel
- Peel- Pectin released from peel residue
- DM- Demethylated Pectin
- Pectin- Commercial pectin demethylated with a papaya extract containing PME activity
- DP- Degree of Polymerization
- GA- Galaturonic Acid

(b)

Figure 7. (a) Preparation of bio-sorbent from biochemical treatment of citrus peel waste. (b) Bio-sorption capacities of different bio-sorbent substrates prepared in (a). Adapted from the information provided in References [89–91].

3. Adsorption Experiments and Mechanism

The bio-sorption of harmful chemicals from wastewaters has been focused on achieving two prime targets: (a) development of novel bio-sorbent substrate material, and optimization of the adsorption process in terms of uptake of pollutant molecules/ions in a batch reactor containing a single target metal, and (b) enhancement of sorption uptake capacity by suitable processing [92,93]. From the viewpoint of carrying out adsorption processes/experiments, either or both of the two main techniques are employed, namely, batch adsorption test and/or column adsorption test. In the batch adsorption process, ion exchange has been identified as the main mechanism for the adsorption and removal of heavy metal ions or dye molecules. The carboxyl and hydroxyl functional groups present on the adsorbent substrate have been demonstrated to play key roles in the adsorption process. Other functional groups, such as amide, sulfonate, phosphate and amino groups, have also been reported to participate in the adsorption process. The adsorption process is a complex interplay between a number of mechanisms, such as complexation, coordination, chelation, ion adsorption or exchange, micro-precipitation, electrostatic interaction, H-bonding and so on. In the experimental part, a fixed amount of bio-sorbent substrate/material is placed with a definite volume of solution containing the pollutant or toxic metal ions/dyes, and stirred/shaken for a specified duration in a beaker or flask. After the adsorption process is completed, the solution is filtered and the adsorbent is regenerated or recycled by washing with water or treating with chemicals, such as acids, alkali or organic solvent(s). Alternately, the bio-sorbent material can also be regenerated by physical or thermo-physical treatments, such as heating, microwaving or sonication [93–95].

In some cases, the test solution has been observed to develop a brown color, which is explained by leaching out of carotenoids from the citrus peel biomass. Carotenoids are responsible for binding the heavy metal ions present in the test solution and forming complexes. The latter has been found to be unable to adsorb onto the bio-sorbent surface, and hence, left in the test solution imparting color. This problem can be solved by chemical pre-treatment of the bio-sorbent material, which helps in leaching out the carotenoid or other colored materials, such as chlorophyll, from the citrus peel biomass. Treating the biomass with isopropanol helps in the removal of soluble compounds without any adverse effect on the nature of biomass material or ion-binding sites on the surface. Citric acid treatment helps in the dissolution of polysaccharides present in the cell wall of the biomass. This facilitates in opening up the physical structure of the biomass and thereby increases the number of adsorption/binding sites, i.e., functional groups. Alkali treatment has been observed to impart a stronger effect on cell wall rupturing and facilitate the exposure of functional groups. Furthermore, the hydroxyl or carboxylic acid groups are converted to their salt forms, thereby helping to enhance the adsorption process by an ion exchange mechanism. An increase in temperature during alkali or acid pre-treatment has been observed in biomass loss. The factors influencing the bio-sorption process are initial pH of the test solution, concentration of the test solution (heavy metal ions, dye molecules, etc.), dosage of adsorbent, pre-treatment of the bio-sorbent, temperature during the adsorption process and duration of the contact time between the sorbent material and the test solution. The advantages of the batch adsorption technique are short analysis time, low operational costs, simple maintenance and conductance and that it can be operated with locally available adsorbent materials with satisfactory efficiency [96].

A next-level technique, which can be employed for large sample sizes or industrial scale purposes regarding adsorption and removal of pollutants, is fixed-bed reactors or the column adsorption method. It is also called a continuous flow column system. The fixed-bed column is a commercially viable technique, and at present, employed in industries fitted with ion-exchange resins or other commercially available adsorbent materials. The column material is usually made of clear-extruded acrylic. The length of the column ranges between 25 and 30 cm with an internal diameter of 1.3–1.5 cm. The bottom layer of the column is filled with spherical glass beads (of diameter 3 mm) to facilitate even distribution of influent flowing across the column length. A fiber screen is placed at the top of the

column to prohibit the scattering of the adsorbent material in the fixed-bed and confine it appropriately in a fixed position during the entire operation. The wet-packing of the column is usually performed in such a way so as to allow a void space inside the column up to 70%. The bed-height is hence adjusted up to 24 cm in order to enhance the length of the fixed-bed, and the column length can be increased by supplementing an additional number of columns in series. During operation, a certain amount of material by weight is wet-packed in the column and the column is conditioned with a suitable solvent (e.g., acidified water of pH 4.0–5.5) overnight. Post-conditioning, the test solution (prepared at the same pH) is percolated through the column at a constant flow rate using a peristaltic pump or a micro-tube pump. The test solution passes through the column contents, i.e., packed adsorption bed, and the latter adsorbs the heavy metal ions or dye molecules, leaving behind the solution with a lesser or minimal concentration of pollutants. If the driving force (concentration variation between sorbent and influent) remains high, the sorbent shows high metal ion uptake. This is due to the adsorbent material being saturated at a relatively high influent concentration, whereas the progressing metal solution comes repeatedly in contact with a fresher and more efficiently adsorbing surface, and thus the effluent leaving the column becomes virtually free of metal ions. The saturated column bed can be regenerated and recycled. Regeneration of the column bed is carried out by eluting the bed with a suitable desorption solution. The effluent samples are collected at a fixed interval of time using a fraction collector [97,98]. The schematic representation of the experimental set-up for the fixed-bed adsorption column is shown in Figure 8. The important reported results of experiments on bio-sorbent materials developed from citrus peel waste are listed in Tables 2–4. The various mechanisms of adsorption of heavy metals and dyes on the biomass derived bio-sorbent surface are shown in Figure 9.

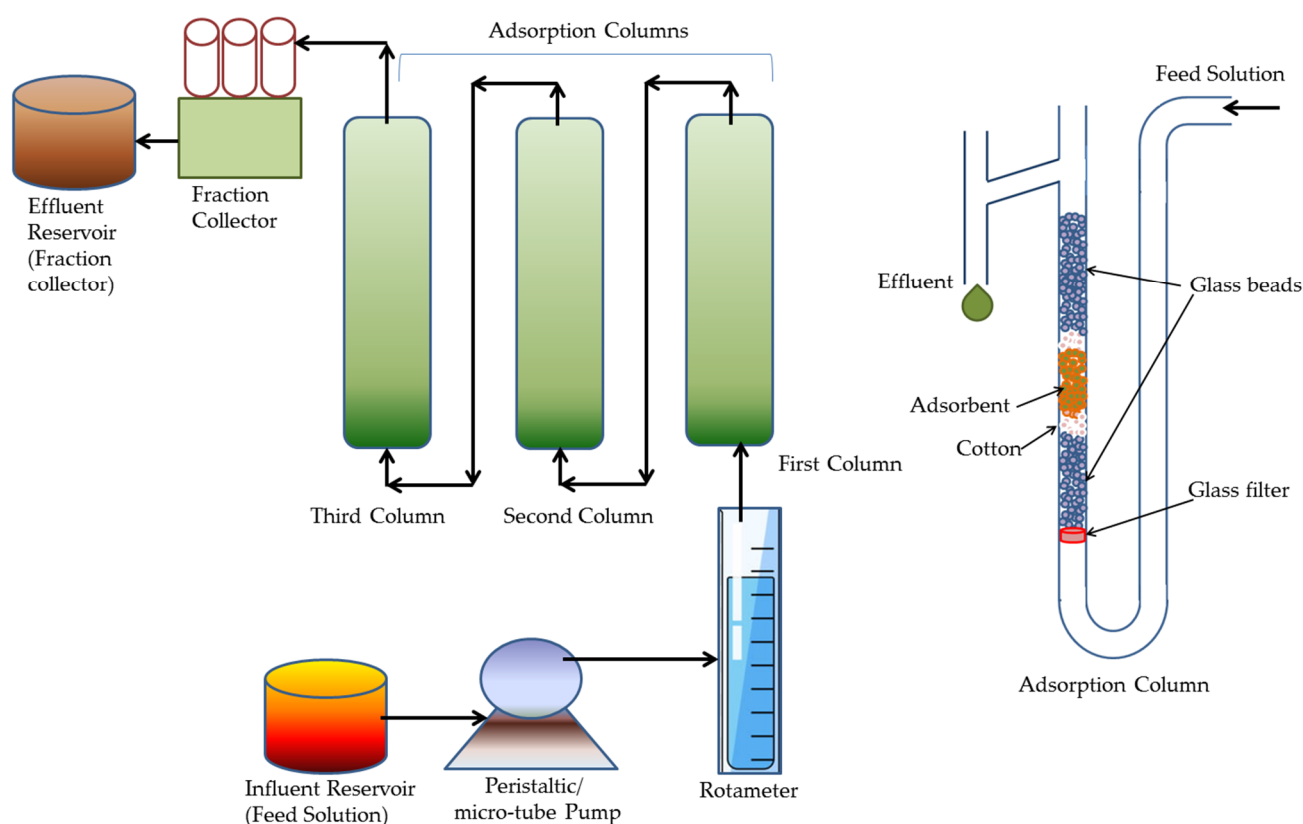


Figure 8. Schematic representation of experimental set-up for fixed-bed adsorption column. Artwork developed from References [97–99].

Table 2. Citrus waste-based bio-sorbents for removal of heavy metals from wastewater (BAT: Batch Adsorption Test; DAT: Direct Adsorption Test (Column Adsorption)).

Adsorbent	Heavy Metals	Processing Method	Maximum Adsorption Capacity (Per Gram Adsorbent)	Ref.
<i>Citrus limetta</i> peels	Uranium	Wash; Dry—333.15 K, 24 h; Grind, P.S. = 850 μm –1.2 mm; BAT—0.1 g BS in 40 mL MS; [U(VI)] = 250 mg/L; pH 2.0–7.0; CT—3 h; SRs—150 rpm	Maximum adsorption of 75.33 mg/g of bio-sorbent material at pH 4.0. Adsorbed species detected are UO_2^{2+} , UO_2OH^+ , $(\text{UO}_2)_3(\text{OH})^{5+}$, $(\text{UO}_2)_2(\text{OH})_2^{2+}$	[100]
<i>Citrus paradisi</i> (Grapefruit) peels	Arsenic	Wash; Dry—333.15 K, 6 h; Grind, P.S.=100–125 μm ; Wash; Dry—333 K, 24 h BAT—0.2 g BS in 15–20 mL MS; [As(V)] = 0.1–50 mg/L; pH 4.0–7.0; CT—15 min–2 h; SRs—100–200 rpm	Maximum adsorption of 37.76 mg/g of bio-sorbent material at pH 4.0, 318 K. 76–94% removal in different polluted water sources	[101, 102]
Orange peels	Nickel	Wash; Dry—373 K, 12 h; Grind, P.S. = 1.80 mm BAT—0.2 g BS in 100 mL MS; [Ni ²⁺] = 10–200 mg/L; pH 5.0; SRs—200 rpm	1.05–29.04 mg/g adsorbent from metal solution of concentration 10–200 mg/L. Maximum adsorbing capacity of 33.14%	[103]
Orange peels	Zinc	Wash; Dry—333.15 K, CW; Grind, P.S. = 0.15–1.5 mm BAT—0.2 g in 50 mL MS, [Zn ²⁺] = 100 mg/L; pH 4.0–6.0; CT—3 h, stirring DAT—Acrylic column, 50 cm length; 2.2 cm diameter; 24 g peel pack, [Zn ²⁺] = 20, 30, 40 mg/L, pH 4.0; FL—8.5 mL/min	BAT—0.664 mmol/g (75%) at pH 6.0 DAT—0.42–0.44 mmol/g	[104]
<i>Citrus reticulata</i> (Ponkan mandarin) peels	Nickel, Cobalt, Copper	Wash; Dry—333.15 K, 24 h; Grind, P.S. $\leq$ 0.6 mm BAT—0.1 g BS in 25 mL MS, [M ²⁺] = 0.01 M, pH = 4.8, Stirring—2 h DAT—50 cm length, 0.5 cm diameter, 1.0 g BS, [M ²⁺] = 5×10^{-4} M, FS—3.5 mL/min, pH 4.8	BAT—Nickel—1.92 mmol/g; Cobalt—1.37 mmol/g; Copper—1.31 mmol/g DAT—Nickel—1.85 mmol/g; Cobalt—1.35 mmol/g; Copper—1.30 mmol/g	[105]
<i>Citrus aurantium</i> (Bitter Orange) fruit parts	Cobalt	Wash; Sundry; Grind, P.S.= 250 μm BAT—2 g BS in 50 mL MS; [Co ³⁺] = 5 mg/L; pH = 2.0, CT = 90 min; stirring	Flavedo = 57.99%; Albedo = 20.11%; Juice = 15.63%; Segment membrane = 20.90%; Seeds = 10.06%	[106]
<i>Citrus reticulata</i> Tangerine	Lanhanum Cerium	Wash; Dry 75–353 K, 24 h; Grind, P.S.= 355 μm BAT—0.5–3 g/l BS; [M ³⁺] = 10–200 mg/L; pH 2.0–6.0; CT = 5–150 min; SRs—200 rpm; T 20–323 K	La(III)—154.86 mg/g Ce(III)—162.79 mg/g	[107]
Ponkan mandarin peels	Lead	Wash; Sun dry—7 d; Grind, P.S. $\leq$ 600 μm BAT—0.2 g BS in 25 mL MS; [M ²⁺] = 0.5–1 g/L; pH 5.0; CT = 120 min; SRs—120 rpm; T 298 K	112.1 mg/g	[108]
Orange waste	Binary systems Cd ²⁺ –Zn ²⁺ Cd ²⁺ –Pb ²⁺ , Pb ²⁺ –Zn ²⁺	Wash; Dry; Grind, P.S.= 0.6–1.5 mm; BAT—0.4 g BS in 100 mL MS; [M ₁ ²⁺ –M ₂ ²⁺] = 15–100 mg/L —15–25 mg/L added subsequently in 30 combinations.	Pb ²⁺ > Zn ²⁺ > Cd ²⁺ Maximum uptake of 0.25 mmol/g adsorbent	[109]
Orange Peels	Chromium	Wash; Dry for 3 weeks; Grind BAT—2 g BS in 250 mL MS; [Cr(VI)] = 0.001 M; CT—5–360 min; Stir—180 rpm	Removal of up to 98% from synthetic chromium solution	[110]

Table 3. Citrus waste-derived bio-sorbents via heat/chemical and enzyme pre-treatment for removal of heavy metals from wastewater.

Bio-Sorbent Modification by Heat/Enzyme/Chemical Treatment (BPT- Bio-Sorbent Pre-Treatment)				
Adsorbent	Heavy Metals	Processing Method	Maximum Adsorption Capacity (per Gram Adsorbent)	Ref.
<i>Citrus limetta</i> peels	Lead	Wash; Dry—343 K, 24 h; Grind, P.S. $\leq$ 1 mm BPT—10% isopropanol, 303 K, 24 h; 1 M citric acid, 303 K, 1 h, 353 K, 1 h; 0.1 M NaOH, 303 K, 6 h, 353 K, 0.5 h; oxidation with 50% H ₂ O ₂ , 353 K, 2 h at pH 11 BAT—0.1 g PTBS in 50 mL MS; [M ²⁺] = 100 mg/L; pH = 4.0, T = 303 K; RSs—100 rpm; CT—6 h	630 mg/g adsorbent. Cold alkali treatment increases adsorption by 87% (80% in first 15 min)	[96]
<i>Citrus tamurana</i> <i>Citrus latifolia</i> peels	Nickel, Cadmium, Lead from <i>Oriza sativa</i> (rice)	Wash; Sundry; Grind, P.S. = 250 μ m; BPT—(a) Soaking in 1% w/v citric acid for 10 min, drained, dried at 423 K, 24 h CTBS (citric acid-treated BS) (b) CTBS heated to 673 K, 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, 298 K, 1 h	Rice soaked with ACPA showed maximum reduction in heavy metal concentration Cd is reduced by 96.4%, Ni by 67.9%, Pb by 90.11%	[111]
Orange, Grapefruit peels	Cadmium	Wash; Dry; Grind, P.S. = 1–1.1 mm; BPT—Protonation —20 g BS in 1 L of 0.1 M HNO ₃ , 240 min stirring, rinsed with DI, dried at 313 K for 740 min, protonated BS BAT—0.05 g protonated BS in 50 mL MS; [Cd ²⁺] = 10–1000 mg/L (0.089–0.89 mM); CT—180 min; pH 5.0	Adsorption of >90% Cd in 50 min. Desorption of the bio-sorbent material using 0.1 M HNO ₃ + 0.1 M Ca(NO ₃) ₂ shows 90% recovery in 60 min	[112]
Orange peels	Cadmium	Wash; Dry; Grind, P.S. = 1–1.1 mm BPT—Protonation—10 g BS in 500 mL 0.1 N HNO ₃ , stirred for 4 h at 120 rpm, 298 K, rinsed with DI till pH 4.0, dried at 318 K for 12 h; PS = 1–2 mm DAT—Acrylic bed column; length 30 cm, diameter 1.3 cm; packed with 5.0 g Protonated BS; Bed height = 24–75 cm; [Cd ²⁺] = 5–15 mg/L; FR = 2–15.5 mL/min; pH 5.5; T = 298 K	0.40 mmol/g adsorbent	[97]

Table 3. Cont.

Bio-Sorbent Modification by Heat/Enzyme/Chemical Treatment (BPT- Bio-Sorbent Pre-Treatment)				
Adsorbent	Heavy Metals	Processing Method	Maximum Adsorption Capacity (per Gram Adsorbent)	Ref.
Orange juice residue waste	Arsenate, Arsenite	Wash; Vacuum dry; Grind, P.S. = 208 μm BPT—Step I—Decolorization: 10 g BS in 500 mL in 80% EtOH, stirred for 24 h, 298 K, filtered, washed with EtOH until colorless Vacuum-dried for 24 h, DBSG (de-colorized bio-sorbent gel) Step II—Cross-linking: 5.22 g DBSG, stirred with 200 mL DMSO for 24 h, 298 K; added 40 mL epichlorhydrin, stirred for 2 h; added 50 mL of 5 M NaOH, stood for 5 h at 323 K; cooled, filtered and washed with 70% EtOH, 0.5 M HCl, again with EtOH to pH 7.0; vacuum-dried, 24 h, cross-linked BS Step III—Phosphorylation: cross-linked BS soaked in 200 mL DMF overnight, filtered and immersed again in 200 mL DMF+ 5.04 g urea; added 3.1 g phosphoric acid drop-wise with constant stirring; stirred for 1 h. Temperature raised to 423 K and stirred for 2 h; cooled to RT, filtered, washed with 70% EtOH and DI until pH 7.0; washed with 0.1 M HCl and DI until pH 7.0; vacuum-dried for 2 days. Phosphorylated BS Step IV—Fe(III) loading: treated with Fe(III) solution of concentration 55.85 mg/L (= 1 mM), Fe(III)-loaded BS BAT—25 mg Fe(III)-loaded BS in 15 mL MS ([Arsenite/ Arsenate] = 15 mg/L, 24 h, T = 303 K) DAT—column packed with 0.1 g Fe(III)-loaded BS and conditioned with pH 4 water overnight. [Arsenate/ Arsenite] = 15 mg/L; FR—0.098 mL/min	Bio-sorbent pre-treatment and Fe(III) loading enables direct removal of arsenite and arsenate together, without oxidizing arsenite into arsenate DAT—0.91 mmol/g adsorbent; 99% removal of arsenic compared to 80% removal by cellulose control DAT—Maximum arsenic adsorbed on the packed bed = 1.1 mg. Elution with 0.1 M HCl recovers 0.62 mg arsenic (60% recovery)	[113]
Orange peels	Cadmium, Copper, Lead	Wash; Sun dry, 6 days; Grind, P.S. = 0.2 mm BPT—Protonation—10 g dried peel soaked in 1 L of 0.1 M HNO₃, 6 h; filtered, rinsed with DI; sun-dried for 6 days. Protonated BS BAT—0.1–1 g protonated BS in 25 mL MS; [M²⁺] = 20 mg/L; CT—5–120 min; T 98 K; pH 5.0. Shaking at 200 rpm	Maximum adsorption of Pb = 73.53 mg/g; Cu = 15.27 mg/g; Cd = 13.7 mg/g. Pb(99.5%) > Cu(89.57%) > Cd(81.03%) at [M²⁺] = 20 mg/L and BS loading of 4 g/L Pb(96.3%) > Cu(93.3%) > Cd(85%) at [M²⁺] = 100–600 mg/L	[114]

Table 3. Cont.

Bio-Sorbent Modification by Heat/Enzyme/Chemical Treatment (BPT- Bio-Sorbent Pre-Treatment)				
Adsorbent	Heavy Metals	Processing Method	Maximum Adsorption Capacity (per Gram Adsorbent)	Ref.
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, 298 K, rinsed with DI until pH = 4.0, dried at 318 K for 12 h; PS = 1–2 mm, protonated BS DAT—Acrylic column; length 30 cm, diameter—1.3 cm, 5 g protonated BS wet-packed. Feed concentration [Pb ²⁺] = 10.36 mg/L; [Cd ²⁺] = 5.62 mg/L; [Zn ²⁺] = 3.27 mg/L. Total feed to the column = 20 L; FR = 9 mL/min, pH 5.0, T = 298 K	Pb (85 mg/g) > Cd (44 mg/g) > Zn (20 mg/g)	[98]
<i>Citrus paradisi</i> (Grapefruit) peels	Zinc, Nickel	Wash; Dry, 323 K until constant weight; Grind, P.S. 0.5–1.0 mm BPT—(a) Blocking of –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 BAT—100 mg BS in 100 mL MS; [M ²⁺] = 300 mg/L, pH 5.0; CT = 120 min; SRs—100 rpm; 298 K	Native peel BS Ni ²⁺ —1.331 meq/g (84.73%) Zn ²⁺ —1.512 meq/g (92.46%) –COOH blocking reduces Ni ²⁺ sorption by 78.57%, Zn ²⁺ sorption by 73.31% –OH blocking reduces Ni ²⁺ sorption by 22.63% and Zn ²⁺ sorption by 28.54%	[69]
Citrus peel pectin	Lead	Citrus peel pectins (a) Low methoxylated (LM) pectin (methoxyl content 9%) and (b) high methoxylated (HM) pectin (methoxyl content 64%) BAT/KS—0.02 g BS in 200 mL MS; [M ²⁺] = 0.1–1.0 mM; pH ≤ 5.0; T 294–298 K; CT—2–1440 min. Background electrolyte concentration—0.01 M NaNO ₃	LM Pectin —0.86 mmol/g HM Pectin —0.87 mmol/g	[115]
Orange waste	Phosphate	Metal-loaded orange waste bio-sorbent: La(III)-loaded, Ce(III)-loaded and Fe (III)-loaded BS BAT—25 mg of La(III)- and Ce(III)-loaded BS and 60 mg of Fe(III)-loaded BS in 15 mL phosphate solution: (Phosphate) = 20–40 mg/L; pH = 7.5 for La(III)/Ce(III)-loaded BS and 3.0 for Fe(III)-loaded BS experiments. SRs = 140 rpm, 24 h, 303 K DAT—Glass column length—20 cm, diameter—0.8 cm; loaded with 150 mg of wet metal-loaded BS, (Phosphate) = 20–40 mg/L; FR = 7 mL/h	Phosphate adsorption by M—loaded BS (% removal) in BAT La(III)-loaded BS —13.84 mgP/g (98.5%) Ce(III)-loaded BS —14.0 mgP/g (98.8%) Fe (III)-loaded BS (99% removal) 13.63 mgP/g adsorbent in DAT	[116]

Table 3. Cont.

Bio-Sorbent Modification by Heat/Enzyme/Chemical Treatment (BPT- Bio-Sorbent Pre-Treatment)				
Adsorbent	Heavy Metals	Processing Method	Maximum Adsorption Capacity (per Gram Adsorbent)	Ref.
Orange waste	Nickel, Cobalt, Cadmium, Zinc	Wash; Dry, 323 K, 72 h. Ball mill—P.S. 0.1–0.2 mm; pore size—30.5 Å, BET surface area—128.7 m ² /g BPT—Different treatments, viz., isopropyl alcohol, alkali saponification, acid oxidation to yield OP, PA, SNa, Sam/SCa, SOA, SCA, SPA; BAT—0.025 g BS in 15 mL MS; [M ²⁺] = 0.001–0.01 M, CT—3 h	SPA—Ni ²⁺ —1.28 mol/Kg (95% increase) SPA—Co ²⁺ —1.23 mol/Kg (178% increase) SCA—Cd ²⁺ —1.13 mol/Kg (60% increase) SOA—Zn ²⁺ —1.23 mol/Kg (130% increase) in comparison to raw orange peel (OP) Zn ²⁺ → SCA>SNa>SOA>SPA>Sam>SCa>OP Cd ²⁺ → SOA>SCA>SPA>SNa>Sam>SCa>OP Co ²⁺ /Ni ²⁺ → SPA>SCA>SOA>SNa>Sam>SCa>OP	[85]
Orange peel	Lead, Zinc, Copper	Wash; Dry, 333.15 K; Grind: P.S. ≤ 0.45 mm –(OP); BET—0.828 m ² /g BPT—100 g dried OP + 500 mL EtOH + 0.8 M NaOH + 0.8 M CaCl ₂ ; soak for 20 h, filter, wash until neutral pH—SCOP; BET—1.496 m ² /g BAT—0.1 g BS (OP and SCOP) in 25 mL MS; [Pb ²⁺] = 200 mg/L; [Zn ²⁺] = 50 mg/L; [Cu ²⁺] = 50 mg/L; SRs—120 rpm; CT—0–12 h; T 298 K	Adsorption capacity SCOP/OP (mg/g) Cu ²⁺ → 70.73/44.28 Pb ²⁺ → 209.8/113.5 Zn ²⁺ → 56.18/21.25 Maximum adsorption was found at pH 5.5 Pb ²⁺ (99.4%) > Cu ²⁺ (93.7%) > Zn ²⁺ (86.6%)	[117]
Orange Peels	Chromium	Wash; Dry, 353 K; Grind, PS ≤ 200 µm BPT—100 g OP + 1 L of 0.1 M NaOH. Soak for 48 h; shake at 120 rpm, filter, wash, dry at 353 K—MOP (BET—0.8311 m ² /g) BAT—0.2–5.0 g MOP in 50 mL MS; [Cr(VI)] = 100 mg/L; SRs—120 rpm; T 298 K; CT = 30 min–4 h; pH 1–8.0	OP → 97.07 mg/g (39.9%) AOP → 139.0 mg/g (41.4%) Maximum adsorption was found at pH 2.0 and BS dose of 4 g/L in 180 min	[118]
Citrus lemon	Cobalt	Wash; Dry, 353 K, 24 h; Grind BPT—Thermal activation in air at 773 K, 1 h. Wash; dry, 373 K, 24 h. PS: BS 150–200 BAT—10 g/1 BS; [Co ²⁺] = 0–1000 mg/L; CT—10 h; SRs—200 rpm; pH 6.0	22 mg/g adsorbent	[119]
Orange waste Peel (OP), Bagasse (OB), Peel-bagasse (OPB)	Lead	Wash; Dry, 333.15 K; Grind, Sieve—BS—100-mesh BPT—1 g BS + 20 mL 0.1 M NaOH, agitation—2 h; Wash, dry—328 K, 24 h. 1 g modified BS + 8.3 mL 1.2 M citric acid; agitation—30 min; filter; dry—328 K, 24 h; heat—393 K, 90 min; Wash; dry—328 K, 24 h BAT—0.5 g BS (OP, OB, OPB)/modified BS (OMP, OMB, OMPB) in 50 mL MS; [Pb ²⁺] = 700 mg/L; pH 2.0–6.0; T = 303 K; CT—10–1440 min	Highest adsorption capacity shown by O-MP—84.53 mg/g OP—55.52 mg/g OB—46.90 mg/g OMB—80.19 mg/g OPB—32.55 mg/g OMP—73.37 mg/g	[120]

Table 3. Cont.

Bio-Sorbent Modification by Heat/Enzyme/Chemical Treatment (BPT- Bio-Sorbent Pre-Treatment)				
Adsorbent	Heavy Metals	Processing Method	Maximum Adsorption Capacity (per Gram Adsorbent)	Ref.
Pomelo Peels	Copper	Wash; Dry, 343 K, 2–3 h. Grind, Sieve—(Pomelo Peel, PP) BPT—PP+ hot acidified water, pH 1.5, T = 388–393 K, 60 min; Filter. The solid peel residue after filtration is de-pectinated pomelo peel or DPP. Washed and dried at 343 K, 2–3 h; Grind: PS—0.42 mm. Filtrate contains pectin, precipitated by 95% EtOH. BAT—0.5 g BS (PP, DPP) + 100 mL MS; [Cu ²⁺] = 25 mg/L; pH = 2.0–6.0; SRs—150 rpm; T 298 K; CT—180 min	Pomelo peel (PP)—19.7 mg/g De-pectinated pomelo peel (DPP)—21.1 mg/g	[121]
Lemon Peel	Cadmium	Wash; Dry—323 K; Grind: PS—0.5–1.0 mm—native peel (NP) BPT—(a) Protonation—10 g NP + 1.0 L of 0.1 M HCl, stir—6 h, 120 rpm; T 298 K; Filter, wash; Dry—323 K—protonated peels (PrP) (b) 10 g NP + 400 mL diluted HCl; pH 1.5 at 358 K; Stir—150 rpm—2 h; T 358 K. Filter: Filtrate is coagulated by 95% EtOH. Wash with 60%, 80% and 95% EtOH with a retention time of 30 min in each washing; vacuum dry—323 K—peel pectic acid (PP) (c) The solid residue left after pectic acid extraction is washed to remove all soluble sugars; vacuum dry—323 K—De-pectinated peels (DPP) BAT—50 mg BS (NP, PrP, PP, DPP) in 50 mL MS; [Co ²⁺] = 100 mg/L (1.78 mequiv./L); pH 5.0; SRs—120 rpm; T 298 K; CT—180 min	Native peel (NP)→ 1.92 mequiv./g Protonated peels (PrP) → 2.44 mequiv./g De-pectinated peels (DPP)→ 1.75 mequiv./g Peel pectic acid (PP)→ 2.86 mequiv./g PP > PrP > NP > DPP	[122]
Orange peels, Lemon Peels, Lemon-based pectin peels (PP)	Cadmium	Native orange and lemon peels → Wash, Dry—311–313 K, 12 h; Grind BPT—Protonation—Lemon-based pectin peels are treated with 0.1 N HNO ₃ , 6 h; Dry for 12 h, 311–313 K; Wash, Dry; Grind— PS: 0.7–0.9 mm—Protonated pectin peels (PPP) BAT—0.1 g BS (NOP, NLP, PPP) in 50 mL MS; [Co ²⁺] = 10–700 mg/L; Shake—6 h; pH 3.0/5.0	0.7–1.2 mequiv./g (39–67 mg/g)	[123]
Citrus Pectin forms	Lead	Different forms of citrus pectins: GA oligomers—Large DP, medium DM and small DP size class GA oligomers (galacturonic acid) PME demethylated pectin (DM—50–80%) Pectin from peel residue Non-calcium-sensitive pectin Lyophilized BS from single-state fermentation of citrus peel (hydrolysis) BAT—50 mg BS in 50 mL MS; [Pb ²⁺] = 0.5–1 g/l; pH 4.5; SRs—120 rpm; T 298 K; CT—6 h	Medium DP size class GA—380 mg/g, small DP size class GA—360 mg/g Large DP size class GA—300 mg/g PME demethylated pectin—220–270 mg/g Pectin from peel residue—140 mg/g Non-calcium-sensitive pectin (NCSP)—200 mg/g Lyophilized BS from fermented citrus peel—100 mg/g	[89]

Table 3. Cont.

Bio-Sorbent Modification by Heat/Enzyme/Chemical Treatment (BPT- Bio-Sorbent Pre-Treatment)				
Adsorbent	Heavy Metals	Processing Method	Maximum Adsorption Capacity (per Gram Adsorbent)	Ref.
Orange Peels	Copper Cadmium	Wash; Dry—343 K, 24 h; Grind: PS—0.45 mm—native peel (NP) BPT—(a) 60 g NP + 300 mL 1% NaOH + 300 mL EtOH; RT; 24 h. Wash; Dry, 343 K, 24 h, DPOP (De-pigmented orange peels) (b) 30 g DPOP + 1 L 1% mercaptoacetic acid, 12 h; Wash; Dry—343 K, 12 h. Grind—PS $\geq$ 0.45 mm BAT—50 mg BS in 10 mL MS; $[M^{2+}] = 0.05\text{--}1$ g/L; SRs—120 rpm; CT—1.5 h; T 298 K, pH—5.0–7.0	Cu ²⁺ —70.67 mg/g Cd ²⁺ —136.05 mg/g	[86]
Lemon Peel	Cobalt	Wash; Dry—333.15 K, 24 h. Grind: PS= 1 mm—native peel (NP) BPT—10 NP + 100 mL 2% IPA, 0.1 N NaOH, 0.1 N HCl, 0.1 N H ₂ SO ₄ , 0.1 N HNO ₃ ; 4 h, 303 K, Wash; Dry—333.15 K, 24 h BAT—0.1 g BS in 50 mL MS; [Co ²⁺] = 100 mg/L, T 303 K, SRs—150 rpm; CT—6 h	Native Peels—20.83 mg/g Modified Peels—35.7 mg/g	[124]
D-limonene	Mercury	Direct reaction between sulfur and D-limonene at (a) 443 K, 1 h; (b) 453 K, 50 mm Hg, 4 h; (c) 373 K < 1 mm Hg, 5 h	55% removal	[125]

Table 4. Citrus waste reuse as bio-sorbents for the removal of poisonous dyes from wastewater.

Adsorbent	Dye	Processing Method	Maximum Adsorption Capacity (Per Gram Adsorbent)	Ref.
<i>Citrus reticulata</i>	Acid Yellow-73	Wash; Sun dry—7 days; Grind; Sieve through 50 ASTM mesh BPT-Soak—10% formaldehyde; air-dried—3 days; Oven-dried—353 K, 2 h BAT—1.0 g BS in 50 mL dye solution; (Dye) = 20 ppm; pH = 3.0; T = 323 K; SRs—100 rpm; CT—65 min;	96.46 mg/g ^{−1} L ^{−1}	[75]
<i>Citrus sinensis</i>	Congo Red, Rhodamine B, Procion orange	Wash; Sun dry—7 days; Grind—PS= 75–500 μ m BAT—250 mg BS in 50 mL Congo Red dye solution; (Congo Red) = 60 mg/L; CT—20–90 min, SRs—140 rpm; T 302 K; pH 5.0 500 mg BS in 50 mL Rhodamine B and Procion orange dye solutions; (Dye) = 10 mg/L; CT—20–90 min, SRs—140 rpm; T 302 K; pH 3.0	Congo Red—22.4 mg/g; pH = 5.0 (76.6%) Procion orange—1.3 mg/g; pH = 3.0 (49%) Rhodamine B—3.22 mg/g; pH = 3.0 (38.43%)	[126]
Grapefruit peels	Methylene Blue	Wash; Sun dry—2 days; Grind—PS > 90 μ m BPT- Carbonization—Treat with (a) BS_ 88% orthophosphoric acid (1: 3 ratio), (b) ZnCl ₂ , or (c) 98% H ₂ SO ₄ Heat at 723–823 K for 0.75–1.5 h, wash with NH ₄ OH and H ₂ O to neutral pH, Dry—12 h; Charred citrus peel (CCF); PS= 135 μ m BAT—0.30–1.0 g CCF in 200 mL MB dye solution; (MB) = 20–100 mg/L; T 303 K; CT—8 h; pH 3.0–10.0	99.08% removal	[72]

Table 4. Cont.

Adsorbent	Dye	Processing Method	Maximum Adsorption Capacity (Per Gram Adsorbent)	Ref.
Orange Peel	Direct Yellow-12	Wash; Dry—423 K, 5 h; Grind BPT—Carbonization—3 kg dried orange peel + 2.5 L 98% H ₂ SO ₄ , Stand—2 h; Boil—3 h; Add to ice-cold water, filter; Dry—453 K, 2 h; immerse in 5.0 L of 5% NaHCO ₃ , wash to neutral pH; Dry—423 K, 3 h; Grind ≤ 0.200 mm BAT—0.5 g in 100 mL dye solution; (Dye) = 75 mg/L; T 300 K; CT—2 h; pH 1.5–11.2; SRs—200 rpm	96% removal	[127]
Grapefruit Peels	Crystal Violet	Wash; Dry—423 K, 5 h; Grind BAT—BS = 0.1–3 g/L of dye solution; (Dye) = 5–600 mg/L; pH 6.0; SRs—100 rpm; T 303 K; CT—60 min	96% removal in 60 min. Maximum adsorption capacity = 254.16 mg/g	[128]
Pomelo Peel	Methylene Blue (Cationic Dye); Acid Blue (Anionic Dye)	Wash; Air dry; Grind-PS: 1.0–2.0 mm BPT—Microwave modification: BS + 1:1.25 by wt. NaOH. Microwave heating at 2.45 GHz, 800 W, 5 min; Wash with 0.1 M DI until neutral pH BAT—0.20 g Modified BS in 200 mL dye solution; (Dye) = 50–500 mg/L; SRs—120 rpm; T 303 K; CT—until equilibrium	Methylene Blue— 501.1 mg/g Acid Blue— 444.45 mg/g	[129]
Pomelo Peel	Congo Red	Wash; Dry—313 K, 48 h; Ball Mill-PS= 0.840 mm BAT—1.0–3.0 g BS in 1 L dye solution; (Dye) = 20–120 mg/L; T 276.15–333.15 K, pH 6.0–8.7; CT- 24 h	0.75–1.08 mg/g	[130]
Citrus medica, Citrus aurantifolia, Citrus documana	Reactive Red 2 (Red M5B)	Wash; Dry—373–393 K, 24 h; Crush BPT—Carbonization—Heat at 773 K, N ₂ ; Liquid phase oxidation with 1 M HNO ₃ ; Wash, Dry—423 K, 12 h BAT—3 g BS in 100 mL dye solution; (Dye) = 20 mg/L; T 298 K; CT = 5–90 min; SRs—120 rpm; pH 3.0–10.0	<i>C. medica</i> → 87% (0.5800 mg/g) <i>C. aurantifolia</i> → 85% (0.5667 mg/g) <i>C. documana</i> → 91% (0.6067 mg/g)	[70]
Citrus limonum	Methyl Orange, Congo Red	Wash; Dry—373 K, 24 h; Grind BPT—Heat at 773 K in air, 1 h; Wash; Dry—373 K, 24 h; PS-BSS 100–250 BAT—0.1 g BS in 10 mL dye solution; (Dye) = 0.3–0.45 mM; T 298 K; CT-until equilibrium; pH 5.5–6.5	Methyl Orange → 50.3 mg/g Congo Red → 34.5 mg/g	[131]
Citrus sinensis bagasse	Methylene Blue	Wash; Dry—333 K, 72 h; Grind-PS: 0.25–0.75 mm BAT—0.1 g in 100 mL dye solution; (Dye) = 50 mg/L; CT—24 h; T 303 K; pH 7.0	96.4 mg/g	[132]
Orange Peel, Lemon Peel	Methylene Blue	Wash; Dry—353 K, 24 h; Grind-PS: <3.0 mm BAT—0.25 g in 25 cm ³ dye solution; (Dye) = 50–1000 mg/dm ³ ; T = 298 K; pH 2.0–3.0	Orange Peel → 4.76–95.03 mg/g Lemon Peel → 4.41–92.1 mg/g	[133]
Grapefruit Peel	Leather Dye mixture: Sella Solid Blue, Special Violet, Derma Burdeaux, Sella Solid Orange	Wash; Dry—333.15 K, 24 h; Grind-PS: <0.5 mm BPT—1.5 g BS + 150 mL of 1 M H ₂ O ₂ ; Stirring—110 rpm, 24 h; Dry; Grind BAT—0.3–1.5 g BS in 50 mL dye solution; (Dye) = 100–400 mg/L; pH 5.5; T 298 K; SRs—120 rpm; CT = 24 h	Untreated Grapefruit peel BS → 45% Modified Grapefruit peel BS → 80% Maximum capacity → 1.1003 meq/g Maximum uptake → 37.427 mg/g	[134]

Table 4. Cont.

Adsorbent	Dye	Processing Method	Maximum Adsorption Capacity (Per Gram Adsorbent)	Ref.
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; Stir and heat at 353 K; 120 min; Cool to RT, add N-vinyl-2-pyrrolidone, stir 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 in air BAT—1:1 BS in 20 mL dye solution; (Dye) = 10–50 mg/L; T = 293–333 K; pH = 7.0 for Congo Red and 6.0 for Methyl Orange; CT (Congo Red) = 6000 min, (Methyl Orange) = 4000 min	Congo Red → 4.8–26 mg/g Methyl Orange → 4.6–10 mg/g	[73]
<i>Citrus grandis</i>	Methylene Blue	Wash; Dry—333.15 K, 48 h; Grind: PS= 0.5–1.0 mm BAT—0.20 g BS in 200 mL dye solution; (Dye) = 50–500 mg/L; pH 7.0; T 303 K; CT = 5.15 h; SRs—100 rpm	344.83 mg/g at 303 K	[135]
Mosambi peels	Erichrome Black T	Wash; Sun dry; Grind; Dry—333 K, 24 h BPT—BS + Concentrated H ₂ SO ₄ (1:1)- 24 h; Dry—378 K, 12 h; Wash with NaHCO ₃ ; Dry—378 K, Mosambi peel activated carbon (MPAC)	93.8%	[136]
<i>Citrus sinensis</i> L.	Remazol Brilliant Blue	Wash, Dry—333 K, 24 h; Grind: Wash, Dry—333 K; PS = 44–1180 µm BAT—300 mg BS in 30 mL dye solution; (Dye) = 30, 100, 250 mg/L; SRs = 150 rpm; T 293–333 K; CT = 24 h	11.62 mg/g	[137]
<i>Citrus sinensis</i>	Reactive Blue 19, Reactive Blue 49	Wash; Dry; Grind—PS < 0.25 mm—BS BPT—(a) Immobilization: BS + sodium alginate (1:2). The resultant beads preserved in 0.02 M CaCl ₂ solution. Immobilized BS (b) 1 g BS + 5% glacial acetic acid. Wash after 1 h; Dry—343 K, 24 h. Acetic acid-treated BS BAT—0.5–1.5 g in 50 mL dye solution; (Dye) = 50–300 mg/mL; CT = 60–120 min; pH 2.0; T 303 K; SRs—100 rpm	Reactive Blue 19 BS → 37.45 mg/g Immobilized BS → 400.00 mg/g Acetic acid-treated BS → 75.19 mg/g Reactive Blue 49 BS → 135.16 mg/g Immobilized BS → 80.00 mg/g Acetic acid-treated BS → 232.56 mg/g	[66]
Citrus waste	Methylene Blue	Wash; Dry; Grind—383 K, 24 h; PS < 0.5 mm BAT—0.70 g in 100 mL dye solution; (Dye) = 5–60 mg/L; T 300 K, CT = 180 min; SRs—120 rpm	3.2994 mg/g adsorbent at (Dye) = 50 mg/L. Maximum removal percentage → 49.35% at 60 mg/L	[138]
Lime Peel	Remazol Brilliant Blue R	Wash; Dry—T 378 K, 24 h; PS= 150 µm BAT—1–9 g BS in 50 mL dye solution; (Dye) = 10–50 mg/L; SRs—120 rpm; CT = 24 h; T 300 K	73–95.89% removal. Adsorption capacity of 7.29–9.58 mg/g	[139]

Table 4. Cont.

Adsorbent	Dye	Processing Method	Maximum Adsorption Capacity (Per Gram Adsorbent)	Ref.
Pomelo Peel	Malachite Green	Wash; Dry—T 393 K, overnight; Grind BPT—Carbonization—973 K, N ₂ , 1 h; Char is soaked in KOH (1:1); Dry—423 K, overnight; Pyrolyze at 1073 K; N ₂ (150 cm ³ /min); At T = 1073 K, CO ₂ flow for 2 h; Cool to RT under N ₂ flux; Wash with 0.1 M HCl; Wash until neutral pH; BET—1357.21 m ² /g BAT—0.2 g BS in 100 mL dye solution; (Dye) = 50–400 mg/g; T 293–333 K; CT = 4 h; SRs = 120 rpm; pH 3.0–10.0	178.48 mg/g Best result at pH = 8.0; T = 333.15 K 95.06% removal	[140]
<i>Citrus reticulata</i>	Indigo Carmine Dye	Wash; Sun dry, 7 days Oven dry—T 343 K, 4 h BPT—(a) 100 g BS + 500 mL 20% formaldehyde, 3 h, FBS (b) 100 g BS + 10% urea solution, 3 h, UBS (a, b)—Filter, air dry; Oven dry, 343 K, 4 h; Grind: Sieve through 50-mesh ASTM = 297 µm BAT—0.3–3.0 g BS in 50 mL dye solution; (Dye) = 25 mg/L; T 293–343 K; CT = 10–70 min; pH 1.0–10.0; SRs—100 rpm	Dried Peel (BS) → 5.90 mg/g Formaldehyde-treated peel (FBS) → 14.79 mg/g Urea-treated peel (UBS) → 71.07 mg/g	[74]
Orange Peels	Acid Violet 17	Wash; Sun dry—4 days; Grind; PS: 53–500 µm BAT—100–600 mg BS in 50 mL dye solution; (Dye) = 10 mg/L; pH 2.0–10.0; CT—80 min; T 303 K	19.88 mg/g; 87% removal at pH = 2.0 and 100% removal at pH = 6.27 at adsorbent dose of 600 mg in 50 mL of 10 mg/L dye solution	[141]
<i>Citrus limetta</i> Peels	Methylene Blue	Wash; Sun dry—4 days; Oven dry—363 K, 24 h; Grind; Sieve, 80 BSS mesh; Wash; Dry—T 378 K, 4 h; Grind; PS= 80–200 BSS BAT—0.05 g in 25 mL dye solution; (Dye) = 25–250 mg/L; CT—3 h; pH 4.0	227.3 mg/g; 97–98% removal	[48]
<i>Citrus sinensis</i> Peels	C.I. Direct Blue 77 dye	Wash; Dry—T 378 K; Grind; PS = 75 µm BAT—5–30 mg in 100 mL dye solution; (Dye) = 50 mg/L; pH 2.0–12.0; SRs = 125 rpm; CT = 60 min	59% removal; 9.43 mg/g	[113]
Orange peel	Methylene Blue	Wash; Dry—343 K, 5 h; Grind; PS= 75 µm, OP (dried orange peel) BPT—60 g OP + 250 mL of 0.1 M NaOH, 24 h; Filter; Wash; Dry—MOP (Modified OP) BAT—0.05 g in 25 mL dye solution; (Dye) = 35 mg/L; SRs = 160 rpm; pH 4.0; CT = 30 min; T 298–318 K	OP → 14.164 mg/g MOP → 18.282 mg/g	[142]

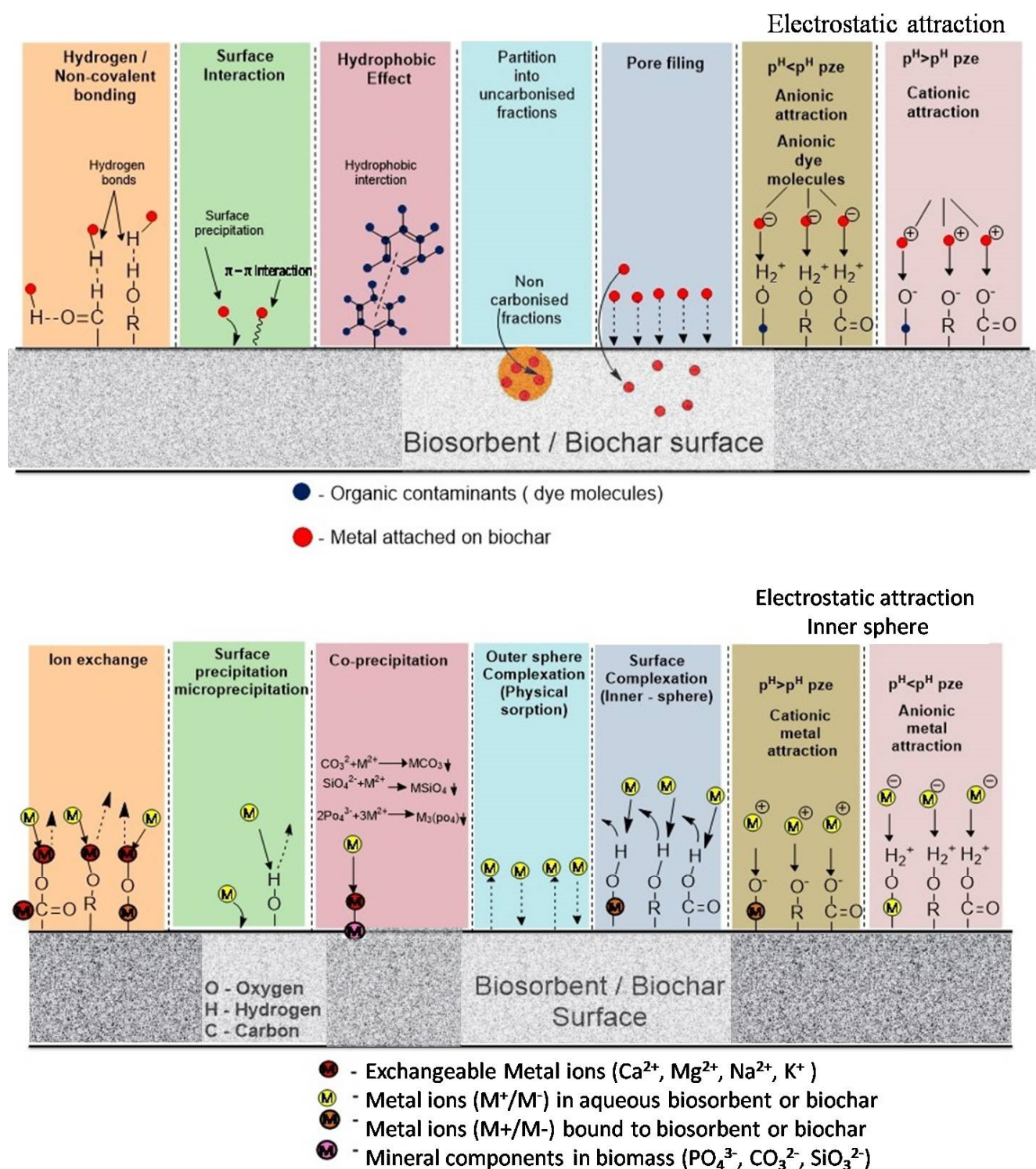


Figure 9. Mechanism of adsorption of dyes and heavy metals from industrial wastewaters by citrus biomass-derived bio-sorbent. Artwork developed from the information provided in [47].

4. Kinetics and Thermodynamics

4.1. Kinetics

The adsorption kinetics helps in defining the rate of efficiency of adsorption. Kinetic parameters are useful for designing and modeling the bio-sorption processes. Several types of kinetic models have been proposed by researchers to study the mechanism and

rate-regulating steps. The Lagergren's rate equation is one of the most commonly used models to explain the adsorption of an adsorbate from the liquid phase [143]. The linear form of the pseudo-first-order equation is given as [144]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

where, ' q_t ' and ' q_e ' are amount of adsorbed material (mg/g) at time ' t ' and at equilibrium, respectively. ' k_1 ' (min^{-1}) is the rate constant for the pseudo-first-order reaction. The pseudo-second-order kinetics explain the involvement of both the adsorbate and adsorbent in the rate-limiting step [113,144]. The equation for the linearized pseudo-second-order reaction is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where, ' k_2 ' is the rate constant ($\text{g/mg}^{-1} \text{min}^{-1}$) of the second-order kinetics [113,145]. The initial adsorption rate ' h ' (mg/g min^{-1}) is defined as:

$$h = k_2 q_e^2 \quad (3)$$

the values of ' k_2 ' and ' h ' can be obtained from the intercept of the plot based on the second-order equation [146]. The kinetics defined by Elovich's model is based on the principle that adsorption sites increase exponentially with progress in the adsorption process, suggesting multilayer adsorption [147]. The linear form of Elovich's equation is given as:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (4)$$

where, ' α ' is the initial rate of adsorption ($\text{mg/g}^{-1} \text{min}^{-1}$) and ' β ' is related to surface coverage (g/mg^{-1}). Weber and Morris proposed an intra-particle diffusion model [117,148]. The equation for the linear form of this model is given as:

$$q_t = kt^{1/2} + C \quad (5)$$

where, ' C ' is the intercept and ' k ' is the intra-particle diffusion constant. The value of ' k ' can be calculated from the slope of the linear plot of ' q_t ' vs. ' $t^{1/2}$ '. If intra-particle diffusion is involved in adsorption, then there would be a linear plot for ' q_t ' against ' $t^{1/2}$ '. In cases where the line passes through the origin, it shows that intra-particle diffusion is the rate-controlling step [132].

4.2. Thermodynamic Observations

Appropriate study and explanation of adsorption isotherms is very significant and crucial for the overall development of the adsorption mechanism and effective design of the adsorption system. It helps to explain the mechanism of interaction between adsorbate molecules with the adsorbent surface. There are many models and operational designs available to understand the batch adsorption system. The most commonly employed methods are Langmuir and Freundlich models. The Langmuir adsorption isotherm model explains monolayer adsorption equilibrium between the adsorbate and the adsorbent [149]. This model is suitable for explaining the chemisorption when there is covalent or ionic bond formation between the adsorbate and the adsorbent. Many systems followed the equation to explain the binary adsorption system. The Langmuir model in its linear form may be expressed as:

$$\frac{1}{q_e} = \frac{1}{K_L C_e q_m} + \frac{1}{q_m} \quad (6)$$

In this equation, ' q_e ' is adsorption capacity (mg/g^{-1}) at equilibrium, ' C_e ' is the equilibrium concentration (mg L^{-1}) of the adsorbate, ' q_m ' is maximum adsorption capacity (mg/g^{-1}) and ' K_L ' is the Langmuir constant (L mg^{-1}). The Freundlich isotherm explains

the multi-layered adsorption phenomenon. It is applicable for reversible adsorption of the adsorbate on the surface of the adsorbent [120,150]. It states that the surface of the adsorbent should be heterogeneous in nature for multilayer adsorption [115,145]. This model states that the surface of the adsorbent has a diverse binding energy spectrum. The linear form of the Freundlich isotherm equation can be expressed as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

where, ' K_F ' is the Freundlich isotherm constant ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$), and shows the adsorption efficiency of per unit mass of adsorbent. The $1/n$ value expresses the heterogeneity factor.

Thermodynamic parameters, e.g., entropy change, enthalpy change and standard free energy, are signification parameters to assess and evaluate the viability of the adsorption process along with the nature of adsorption. The negative value of change in enthalpy (ΔH°) shows the exothermic nature of the adsorption process, while the positive value of change in entropy (ΔS°) stipulates the increased randomness of the process at the interface. It explains that the process is entropy-driven. The Gibbs free energy change of the adsorption process is subsequent to ' K_c ' and given by the following equation:

$$\Delta G^\circ = -RT \ln K_c \quad (8)$$

Here, ' K_c ' can be expressed as shown in the following equation:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

Standard free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) can be determined by using the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (10)$$

where, ' R ' is universal gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$), ' T ' is temperature in Kelvin and ' K_c ' is equilibrium constant. Change in enthalpy (ΔH°) and entropy (ΔS°) can be calculated from the slope of the plot of (ΔG°) vs. T . Reported values of ΔH° for physical adsorption range from -4 to $-40 \text{ kJ} \cdot \text{mol}^{-1}$. Bhatnagar et al. has calculated thermodynamic parameters to check the adsorption nature of cobalt using lemon peel as a bio-sorbent. The value of ΔH ($-21.2 \text{ kJ} \cdot \text{mol}^{-1}$) found in the range shows the physical adsorption [119]. The value of ΔG calculated indicates the spontaneity in the process. A thermodynamic study of the bio-sorption of methylene blue from *C. sinensis* bagasse was observed by Bhatti et al., and the calculated value of ΔH° (51.9 kJ/mol) shows a similar physical adsorption in the process as a purely physical or chemical one [132]. The role of physisorption can be explained on the basis of the heat involved, which is $>40 \text{ kJ} \cdot \text{mol}^{-1}$, whereas, for chemisorption, it is reported in a range of 80 – $200 \text{ kJ} \cdot \text{mol}^{-1}$. Similar results have been reported for the adsorption of Reamzol Brilliant Blue using an orange peel adsorbent [137]. The process was efficient as the negative value of free energy denotes the feasibility of the process. Additionally, the positive values of ΔH and ΔS shown are in favor of the adsorption process. These results also show the affinity of the adsorbent towards the dye. However, the adsorption of dyes has been reported as an exothermic phenomenon in many studies. Bio-sorption of La and Ce using peels of *Citrus reticulata* was also found to be a thermodynamically feasible and spontaneous process. It is shown to be a process of endothermic nature in the temperature range of 293 – 323 K , and the overall entropy increases due to the exchange of the metal ions with more mobile ions [107]. Malachite green dye adsorbed by *Citrus grandis* peels revealed the change in ΔG° from -21.55 to $-24.22 \text{ kJ} \cdot \text{mol}^{-1}$, in the temperature range of 303 to 333 K , indicating enhanced spontaneity at high temperatures [140]. Similar results were also observed during the removal of fluoride using a *Citrus limetta* peels adsorbent activated with FeCl_3 [56]. A thermodynamic study for the removal of methylene blue dye

using *Citrus limetta* peel waste exhibited Gibbs free energy (ΔG°) values in favor of the process [48] (Table 5). Kaffir lime peels were used to reduce graphene oxide to prepare reduced graphene oxide (RGO), and applied for the absorption of methylene blue [151]. Several kinetic models fitted for the citrus peel as adsorbent have been shown in Table 5.

Table 5. Thermodynamics and kinetics studies of various dyes and ions on citrus peel as adsorbents.

Citrus Peel as Adsorbent	Adsorbing Substance	T (Kelvin)	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	Isotherm Fitted	Kinetics Model	Ref.
Lemon peel	Cobalt	298, 318	−37.47, −38.56	−21.2	54.61	Langmuir model	Pseudo-second-order	[119]
<i>Citrus sinensis</i> (Musambi peel)	Methylene Blue dye (MB)	303, 308, 313, 318, 323	0.76, 2.40, 2.90, 3.90, 4.40	−51.9	−0.18	Langmuir model	Pseudo-second-order	[132]
<i>Citrus sinensis</i> (Orange peel)	Brilliant Blue dye (BB)	303, 313, 323, 333	−14.70, −16.11, −17.59, −18.32	22.82	124.20	Langmuir and Freundlich isotherms	–	[137]
<i>Citrus sinensis</i> (Orange peel)	Arsenic	293, 298, 303, 308, 313, 318	−30.18, −32.42, −33.35, −34.48, −35.06, −35.66	30.0	−0.21	Langmuir isotherm	Pseudo-second-order	[102,121]
<i>Citrus grandis</i> (Pomelo peel)	Malachite Green dye (MB)	303, 318, 333	−21.55, −22.89, −24.22	9.16	0.15	Langmuir isotherm	Pseudo-second-order	[140]
<i>Citrus maxima</i> (Pomelo peel)	Copper	298, 308, 318	−5.38, −4.19, −3.49	−32.18	0.09	Langmuir isotherm	Pseudo-second-order	[121]
<i>Citrus limetta</i> (Musambi peel)	Methylene Blue dye (MB)	293, 303, 313, 323	−7.87, −9.38, −10.49, −12.41	35.13	146.70	Langmuir isotherm	Pseudo-second-order	[48]
<i>Citrus limetta</i> (Musambi peel)	Fluoride	298, 308, 318	−0.69, −3.45, −5.61	72.58	246.22	Langmuir isotherm	Pseudo-second-order	[56]
<i>Citrus limetta</i> (Musambi peel)	Chromium	303, 313, 318, 323, 328	−420.21, −725.16, −726.24, −2044.33, −1151.51	1.914×10^{-3}	57.44	D-R isotherm	Pseudo-second-order	[152]
rGO-Kaffir Lime Peel Extract	Methylene Blue dye (MB)	303, 313, 333	−5.98, −6.81, −8.47	19.15	82.93	Langmuir isotherm	Pseudo-second-order	[151]
Magnetite Orange peel	Crystal Violet	303, 313, 323, 333	−5.92, −6.95, −8.02, −9.35	28.02	111.60	Langmuir isotherm	Pseudo-second-order model	[153]
Lemon peels impregnated with phosphoric acid	Erythrosine-B (EB) Rhodamine-B (RB)	298 298	−3.19 −2.97	27.43 24.41	102.76 91.87	Langmuir model	Pseudo-second-order model	[154]
Orange (<i>Citrus sinensis</i>) peels by acid activation	Methylene Blue dye (MB)	313, 323, 333	−20.5, −12.9, −15.4	67.60	281.70	Langmuir model	Pseudo-second-order model	[155]

5. Design of Experiments

Response surface methodology (RSM) is a very popular tool for the optimization of process variables. It has been adopted in various studies for the design and analysis of the experiments. Principally, it is a mathematical and statistical technique for the design of experiments using relations between a cluster of controlled experimental variables and the measured properties, created on one or more selected conditions [156]. Numerical or physical experimental data are calculated by an expression that is generally a low-order polynomial. Usually, a second-order polynomial equation is fitted to analyze the experimental data by means of RSM, which can be represented as:

$$Y = b_0 + \sum_{i=1}^n b_i x_i + \left(\sum_{i=1}^n b_{ii} x_i \right)^2 + \left(\sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} x_i x_j \right) + \epsilon \quad (11)$$

The results are obtained as 2D contours and 3D plots. This method is very competent, and uses the experimental data and interactions between the factors [157,158]. This process

is based on three key steps, which involve statistically designed experiments, determination of the coefficients through estimation of response via mathematical modeling and investigating the competency of the model [159]. The ANOVA program is used to calculate the statistical parameters along with the optimization of independent parameters and dependent output responses. Dutta et al. analyzed the result of each run and correlated the responses with three individual factors for preparation of an adsorbent using an empirical second-degree polynomial, as shown above. Optimized conditions obtained as responses for carbonization of citrus fruit peel were weight ratio of the peel to the activating agent, temperature of carbonization and time of carbonization, which have the values of 3:1, 798 K and 0.75 h, respectively (Table 5) [72]. An experimental design for the removal of MB dye by charred citrus fruit peel has also been attained. Numeric parameters selected were initial concentration of MB, amount of adsorbent and pH of the solution, and results obtained from statistical design were maintained during the experiment and found to be fitted for the removal of dye [72]. The model adequacy of the Cr(VI) adsorption by Musambi peels was also found to be statistically viable [152]. In recent years, RSM modeling has been applied and reported in several adsorbent-based materials. It is an efficient and useful procedure which can help maximize the performance along with responses based on combinations of variables. Therefore, RSM offers an extensive scope for modeling the parameters' optimization along with the percent removal of heavy metal/dye by citrus peel waste-based adsorbent materials. Some of the experimental models applied for citrus peel adsorbents are recorded in Table 6.

Table 6. Applications of RSM in the bio-sorption process.

Object of Experimental Design	Independent Variables	Response(s)	Remarks	Ref.
Parameters optimized for the preparation of adsorbent from citrus fruit peel	Weight ratio (citrus fruit peel to activating agent), temperature of carbonization	Operating parameters for carbonizing of citrus peel	Optimized conditions for carbonization of citrus fruit peel are: weight ratio of peel to activating agent (3:1) at temperature of 798 K, and time of carbonization was 0.75 h	[72]
Citrus fruit peel used in the removal of methylene blue (MB) dye	Initial concentration of MB, weight of CCFP and pH	Percentage removal of MB	99.6225% MB removal at pH 3.64, weight of CCFP. Initial concentration of MB kept constant at 0.65 g and 20 mg/L. Prepared adsorbent is superior in terms of its porosity.	[72]
<i>Citrus limetta</i> peel dust used for removal of Cr(VI)	Initial concentration and pH of solution	Cr(VI) adsorption by musambi peel	Initial concentration 6.75, pH 4.29, dose 0.27 g/100 mL and contact time 56.40 min	[152]
Adsorption of Brilliant Green (BG) dye by adsorbent prepared from <i>Citrus limetta</i> peel	Temperature, pH, adsorbent dosage and contact time	Percentage removal efficiency of BG	The model validations as optimum levels of the process parameters to obtain the maximum adsorption of dye of 85.17% at 313 K, pH 9, at an adsorbent dose of 3.5 g/L of aqueous dye solution and contact time of 240 min	[160]
Adsorption of Eosin Y by the activated carbon (WCAC) prepared from waste citrus peel	Concentration of Eosin Y, temperature and the adsorbent dose	Adsorption of Eosin Y	Maximum dye uptake of 59.3 mg/g at the dye concentration of 50 mg/L, temperature 333 K and the adsorbent dose of 0.1056 g	[161]
Adsorption of antibiotic Trimethoprim studied by activated carbon prepared from waste citrus peel (WCAC)	Concentration of solution, pH, temperature and adsorbent dose	Adsorption efficiency of trimethoprim by WCAC	Maximum adsorption amount of TMP by WCAC calculated was 144.9 mg/g at 293 K	[162]

6. Summary and Conclusions

Biotransformation of citrus waste into valuable compounds and adsorbent substrate materials for the purpose of adsorption of heavy metals, dyes and toxic chemicals from industrial wastewaters is among hugely adopted research projects around the world. Hazards of pollution in water are not only restricted to the aquatic ecosystem but are also found to spread to the underground water tables, crops and crop products, human/livestock/birds' health and microbial ecosystems on the land. Adsorbents from citrus wastes can be developed by a number of methods, namely physical processes, chemical methods, thermal and thermo-chemical techniques. Protonated adsorbents have demonstrated efficiencies better than native peel bio-sorbents. In addition, chemically treated bio-sorbents exhibit several advantages, such as greater chemical and mechanical stabilities in the test solution. Furthermore, they help in improving the surface properties with additional functional groups or active adsorption sites and enhance the adsorptive capacities of the resultant sorption materials. Thermochemical activation gives rise to activated carbon materials, which show enhanced porosity to facilitate physisorption along with chemical adsorption. The sorption process is governed by a number mechanisms, such as physical adsorption on the adsorbent surface by van der Waals forces of attraction, hydrogen bonding, dipole-induced dipole moments and electrostatic attraction between charged species, i.e., cationic charges on heavy metal ions and polyanionic charges on the bio-sorbent surface. Two main methods of carrying out sorption processes are popular and widely adopted in experiments: batch adsorption tests and fixed-bed adsorption columns. The latter has an advantage of installing an additional number of columns in order to increase the length of the adsorption bed for enhanced capacity of removal of pollutants from wastewater. Theoretical studies, including kinetics, thermodynamics, simulation and modeling, add a greater in-depth understanding of the adsorption mechanism. Bio-sorbents derived from citrus wastes, the largest fruit crop grown on the planet, provide an inexpensive, natural, renewable and sustainable means of obtaining resourceful as well as fruitful products.

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