

Review Article

Applications of Bio-waste Materials as Green Synthesis of Nanoparticles and Water Purification

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Abstract: Towards the future of green, sustainable and renewable products the suggestion of using the agriculture biomass in the coming decades got increased. Biomass material is one of the important sources of alternative material for the production of biocomposite products. An increasing global awareness about environmental issues is acting as the driving force behind the utilization of biomass material as valuable products. Bio-waste materials (agricultural waste) have been recognized as an ecological burden for the society they stimulated new gateways for the production of renewable, low cost and sustainable adsorbents for water treatment applications. In the area of water purification, nanotechnology offers the possibility of an efficient removal of pollutants and bacteria. Adsorption has proved that it is the best process of water treatment technologies, because of its significant advantages. Different modification methods of waste-based adsorbents, have also been presented to highlight and discuss the key advancements on the preparation of novel adsorbents using agricultural “agro-waste”. Adsorption mechanisms responsible for pollutants removal by waste-based adsorbents have also been discussed. It also focuses on the computational aspects of binding of biomolecules to nanoparticles (NPs) and some of the applications of the biosynthesized NPs as water purification. The nature acts like a large “bio-laboratory” comprising of plants, algae, fungi, yeast, etc. which are composed of biomolecules. These naturally occurring biomolecules have been identified to play an active role in the formation of nanoparticles with distinct shapes and sizes thereby acting as a driving force for the designing of greener, safe and environmentally benign protocols for the synthesis of NPs. The biosynthesis of NPs using waste materials will help researchers not only to design safer nanomaterials but also to promote the understanding of health and safety considerations of NPs. Useful materials can be produced easily even at reasonable scale because the biomaterial based routes eliminate the need to use toxic chemicals. The aim of this review is to summarize the adsorption capacities for organic and inorganic pollutants by different bio-waste-based adsorbents.

Keywords: Bio-waste, Agricultural Waste, Green Synthesis, Nanoparticles, Water Purification, Low Cost Adsorbents

1. Introduction

Water is declined sharply worldwide in the previous few decades, at the present time; water is facing a number of risks such as pollution and salination. The main sources of water pollution are leakage of untreated spotless and toxic industrial wastes, throwing of industrial flow, and fled from the agricultural fields along with others. In the recent years, different toxic chemicals/compounds (e.g., micropollutants,

personal care products, endocrine disrupting compounds, inorganic, pesticides, anions etc.) which necessitates the need for attention and rationalize consumption and work on the development and preservation of the water resources [1].

A variety of remediation technologies are available with variable degree of success to control water pollution [1]. However, the short comings of most of these methods are high maintenance and operational costs, generation of toxic ordure and complicated procedure involved in the treatment.

Comparatively, absorption process is considered a better alternative in the water treatment by reason of convenience, ease of operation and simplicity of design [2]. Further, this process can remediate varied type of pollutant of organic and inorganic compounds and thus, it has a wider applicability in water remediation. Stimulated carbon is undoubtedly considered as universal adsorbent for streaming remediation and is commonly used to treat Contaminants from water. However, its prevalent use in wastewater curing is sometimes restricted due to its higher cost. A large variety of low-cost adsorbents has been examined for their ability of removal wide-ranging kinds of pollutants from wastewater and water and has been reviewed widely [3].

Activated carbon is the mostly-used adsorbent; nevertheless, it is relatively expensive among other sorbents and its usage depends on the degree of the required treatment process and the local availability of activated carbon [4].

Biosorption is the uptake of metal ions and radionuclides from aqueous environments by biological materials, such as algae, bacteria, yeast, fungi, plant leaves and root tissues, which can be used as biosorbents for detoxification and recovery of toxic or valuable metals from industrial discharges [5]. It has many advantages including low capital and operating costs, selective removal of metals, biosorbent regeneration and metal recovery potentiality, rapid kinetics of adsorption and desorption and no sludge generation. Biosorption technology has been shown to be a feasible alternative for eliminating heavy metals from wastewater [6]. Certain waste materials from industrial or agricultural operations may be potential alternative biosorbents [7]. Agricultural waste materials being economic and ecofriendly due to their unique chemical composition, availability in abundance, renewable, low in cost and more efficient are seem to be viable option for organic and inorganic treatment. These promising agricultural waste materials are used in the removal of contaminant either in their natural form or after some physical or chemical modification. But, many studies have shown that the adsorption capacity of these adsorbents may be increased by their treatment with chemical reagents [8]. In general, raw lignocellulosic biosorbents were modified by various methods to increase their sorption capacities because metal ion binding by lignocellulosic biosorbents is believed to take place through chemical functional groups such as carboxyl, amino, or phenolics. More recently, great efforts have been contributed to modify and improve new adsorbents. Many investigators have studied the feasibility of using low-cost agricultural based waste materials.

2. Bio-waste Materials as Adsorbent of Contaminate from Waste Water

Agricultural by-products could be inorganic and organic adsorbents which could be also selective for some metal ions [9]. Agricultural material such as banana and orange peels. [10] Bagasse pith, sawdust wastes [11], maize cob, coconut husk fibres [12], nut shells [13], soybeans and cotton seed hulls

have been evaluated for their adsorptive properties. These materials have been reported to adsorb different pollutants such as heavy metal ions, dyestuff and other toxic pollutants [14], have been evaluated for the adsorption of heavy metal ions from wastewater. Research in the use of agricultural by-products [15] has included metal binding studies with Daturainnoxia, dyed cellulosic materials, wheat and rice bran, oat fiber, sugarcane bagasse, maize cob [16] and sawdust to mention a few [17]. By using natural agricultural waste fibers, the adsorption of pollutants from aqueous solutions can be much more economical with regard to other similar physico-chemical processes.

Agro-waste materials are usually composed of lignin and cellulose as the main constituents. Other components are hemicellulose, extractives, lipids, proteins, simple sugars, starches, water, hydrocarbons, ash and many more compounds that contain a variety of functional groups present in the binding process. Cellulose is a crystalline homo-polymer of glucose with β 1-4 glycosidic linkage and intramolecular and intermolecular hydrogen bonds. Hemicellulose is a heteropolymer of mainly xylose with β 1-4 glycosidic linkages with other substances of acetyl feruoyl and glycouronyl groups. Lignin is three dimensional polymer of aromatic compounds covalently linked with xylans in hardwoods and galactoglucmannans in softwoods [18].

The functional groups present in biomass molecules like acetamido groups, carbonyl, phenolic, structural polysaccharides, amido, amino, sulphhydryl carboxyl groups alcohols and esters have the affinity for metal complexation. Some biosorbents are non-selective and bind to a wide range of inorganic such as heavy metal with no specific priority. The presence of various functional groups and their complexation with heavy metals during biosorption process has been reported by different research workers using spectroscopic techniques that facilitate metal complexation which helps for the sequestering of heavy metals. Many researchers have done the research on using agricultural waste in adsorption of heavy metals. It has been reported that wood wastes such as sawdust, barks and tree leaves effectively remove cadmium species from aqueous systems [19]. The binding mechanisms of heavy metals by biosorption could be illustrated by the physical and chemical interactions between cell wall ligands and adsorbents by ion exchange, complexation, coordination, chelation, physical adsorption and micro-precipitation [20]. The diffusion of the metal from the bulk solution to active sites of biosorbents predominantly occurs by passive transport mechanisms and various functional groups such as carboxyl, hydroxyl, amino and phosphate existing on the cell wall of biosorbents which can bind the heavy metals. Tree leaves from agricultural operations have generally little or no economic value [21]. Cost is an important parameter for comparing the sorbent materials [22]. By-products of soybean and cottonseed hulls, rice straw and sugarcane bagasse were evaluated as metal ion adsorbents in aqueous solutions [23]. They had reported that the modified rice husks are a potentially useful material for the removal of lead from aqueous solutions. The rapid removal and high adsorption

capacity make it very attractive alternative adsorption material. Rice husks contain a high proportion of cellulose (28-36%), thus it appears to be a good candidate for modification with carboxylic acids. The addition of carboxyl functional groups may enhance the sorption capacities of the rice husks.

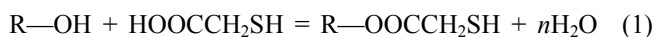
Activated carbon prepared from rice husk, ground nut husk, fertilizer waste slurry, peanut hull, jute stick, moringa olefera seed husk, coconut husk and sawdust have been used for wastewater treatment and the potential of their ultimate usage may be examined by their adsorption capacity, regeneration characteristics and physical properties of subsequent products. In recent years, adsorption has emerged as a cost-effective and efficient alternative for removing heavy metals from low strength wastewaters [24]. Rice husk are an agricultural waste produced in excess of 100 million tons as a by-product of the rice milling industry of which 96% is generated in developing countries. The utilization of this source of biomass would solve some disposal problem as well as access to cheaper materials for adsorption in water pollutants control system [25]. Since the main components of rice husk are carbon and silica (15-22% SiO₂ in hydrated amorphous form like silica gel), it has the potential to be used as an adsorbent [26]. When rice husk is burnt, about 20 wt% of the husk remains as ash. The rice husk ash has more than 95 wt% of silica with high porosity and large surface area, because it retains the skeleton of cellular structure. These properties of the rice husk ash could be used to synthesize siliceous raw materials such as clay materials [27].

Among the natural materials and agro-waste by-products used in the adsorption of heavy metals from aqueous solutions are pumice, charcoal and banana peels. Previous studies conducted have also shown that these materials have effective adsorption for heavy metals including Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ [28]. Pumice is a volcanic stone which has a low weight, a porous structure of up to 85%, and can be found in many regions of the world [29]. The use of pumice as an adsorbent to remove metals from wastewater treatment at low cost is a well-established process [30]. Recently, many researchers have used pumice for removal of heavy metals including cadmium, nickel and copper [31]. Zeolitized pumice was able to adsorb six metallic cations of Cu²⁺, Ni²⁺, Zn²⁺, Cd²⁺, Pb²⁺ and Cr³⁺ showing removals of metal ions between 100 and 500 mg/g in a short time and the concentration lowered under the legal limits [32]. The use of fruit peels in adsorption of heavy metals have also been investigated including banana and orange peels [33]. The advantages of using fruit peels as the adsorption material is that they are readily available and less costly [34].

The ability of fruit waste of orange to remediate Zn, Ni, Cu, Pb and Cr from aqueous solution by absorption was examined [35]. The absorption was in the order of Ni(II) > Cu(II) > Pb(II) > Zn(II) > Cr(II). The absorption of Ni(II) is pH dependent and maximum elimination happens at pH 6. Desorption was possible with 0.05 M HCl and was found to be 95.83% in column and 76% in batch process, consecutive. The spent adsorbent was remade and reprocessed thrice. The elimination and recovery was also done in wastewater and was

found to be 89% and 93.33%, Consecutive. Orange peel waste amendment with varied chemical reagents as biosorbents were used to uptake cadmium ion from water solution [36]. First crude dried orange peel was ground in ball mill to obtain smaller particles of approximate size between 0.1 and 0.2 mm which were used in the experiments. Its intermediate pore diameter was 30.5 Å and definite surface area was 128.7 m²g⁻¹.

Effects of varied chemical amendment including washing, alkali saponification, cross-linking temperature and concentration of cross-linking reagent on the biosorbent properties were investigated. It was deduced that cadmium ion could be eliminated by 0.6SCA80 (orange husk modified with 0.6 mol/L citric acid under 80°C after alkali saponification) biosorbent effectively and quickly. For 0.6SCA₈₀, the maximum ability of cadmium was 0.90 mol/kg, the ideal pH value was 6, the reaction balance was created after a shaking time of 120 min and the ideal solid/liquid ratio was 4.3 g/L. The uptake rate of cadmium was 94% with 0.15 mol/L HCl solution. The preparation of chemically modified orange peel cellulose adsorbents and its biosorption behaviors of Co(II), Ni(II), Zn(II) and Cd(II) have been examined [37]. The elemental analysis of raw orange husk showed that it is composed of 42.2% carbon, 5.4% hydrogen, 51.4% oxygen and 1.0% nitrogen. Effects of varied chemical modifications including varied alkalis saponification (NaOH, NH₄OH, and Ca(OH)₂) and varied acids (C₆H₆O₇.H₂O, H₂C₂O₄, and H₃PO₄) modulation after saponification with NaOH (SNa) on the adsorbent properties were investigated. Fourier transform infrared spectroscopy (FTIR) spectra showed that there were varied functional groups in adsorbents, which were able to react with metal ions in aqueous solution. The maximum absorption capacities of Ni(II), Co(II), Zn(II) and Cd(II) for SPA (orange peel waste modified with phosphoric acid after SNa), SCA (orange husk modified with citric acid after SNa) and SOA (orange husk modified with oxalic acid after SNa) were acquired as 1.28, 1.23, 1.21 and 1.13 mol/kg and have increased by 95, 178, 60 and 130% compared to raw orange husk, respectively. FT-IR spectra revealed that the functional groups responsible for metal biosorption were the -OH, -COOH and -NH₂ groups on the surface. The chemically modified orange husk was prepared from hydrolysis of the grafted copolymer, which was synthesized by interaction of methyl acrylate (MA) with cross-linking orange peel [38]. The chemical remediation involved pretreatment of orange husk with NaOH solution; followed by leaching with mercapto-acetic acid (C₂H₄O₂S) in order to convert its abundant hydroxyl groups into mercapto groups which have a high affinity for metal ions, thereby improve its absorption ability according to the reaction shown below:



The results of element analysis of C and S on infrared C-S analyzer showed that after chemical modification, C% decreased from 43.24% to 36.94%, and S% increased from 0.12% to 0.19%, which means that some hydrocarbons were removed and sulfur atom was chemically bonded and/or

physically adhered to the surface of OP. Maximum absorption capacities of Cu^{2+} and Cd^{2+} on the mercapto-acetic acid modified orange husk were found to be 70.67 and 136.05 mg/g, respectively. Adsorption-desorption studies showed that the mercapto-acetic acid modified orange peel could be used for more than five cycles. Orange Peel (OP) biosorbents were characterized by different analytical techniques, which confirmed that carboxylic groups were introduced into the orange husk by chemical modulation [citric acid (CO), saponification and citric acid (SCO)] and that Cyanex 272 was successfully immobilized on the orange husk (272OP, 272CO, and 272SCO). In addition, Cyanex 272 played an important role in the absorption process, i.e., the maximum absorption ability was improved, with the order of the absorption capacities being $272\text{SCO} (1.30 \text{ mol/kg}) > \text{SCO} (1.26 \text{ mol/kg}) > 272\text{CO} (1.20 \text{ mol/kg}) > 272\text{OP} (1.02 \text{ mol/kg}) > \text{CO} (0.62 \text{ mol/kg})$, and the equilibrium time was shortened from 60 to 40 min for 272SCO. adsorption of $\text{Pb}(\text{II})$ was found to be strongly dependent on pH, with the ideal pH range being 5.0–5.8 for all adsorbents, and the elimination rate of $\text{Pb}(\text{II})$ by 272SCO could be as high as 100%. The ideal solid/liquid ratio was 3.7 g/L for an initial $\text{Pb}(\text{II})$ concentration of 0.002 mol/L. The ideal desorption agent was found to be 0.1 mol/L HCl. The absorption ability of 272SCO declined slightly after being recycled six times. After the sixth cycle, the absorption rate of $\text{Pb}(\text{II})$ onto 272SCO was still 89.61%. Orange Peel (OP) was modified by KCl to prepare a novel orange husk adsorbent named as KOP [39]. The absorption behaviors of KOP for five heavy metals (Cu^{2+} , Cd^{2+} , Pb^{2+} , Zn^{2+} , Ni^{2+}) were studied. All absorption processes can attain equilibrium with 20 min and kinetics data of five heavy metal ions were fitted to pseudo-second-order model. The maximum absorption capacities for Cu^{2+} , Cd^{2+} , Pb^{2+} , Zn^{2+} and Ni^{2+} were calculated as 59.77, 125.63, 141.84, 45.29 and 49.14 mg/g, respectively. Recycle and reuse experiments indicated that KOP could be used for more than ten cycles. Sulfured orange peel (MOP) was used as adsorbent to examine its absorption behaviors of Pb^{2+} and Zn^{2+} from aqueous solutions [40].

The maximum Langmuir absorption capacities for Pb^{2+} and Zn^{2+} elimination by MOP were evaluated as 164 and 80 mg/g, respectively. The sulfured orange husk can adsorb metal ions through ion exchange, or complexation, or by a combination of both processes. Orange waste powder (OPP) was successfully modified into a novel magnetic Nano-adsorbent (MNP-OPP) by co-precipitating it with Fe_3O_4 nanoparticles (MNP) for cadmium ion elimination from aqueous solutions. The BET surface area of OPP, MNP and MNP-OPP was found to be 47.03, 76.32 and $65.19 \text{ m}^2\text{g}^{-1}$ respectively. Authors pointed out that although MNP-OPP had a lower surface area than MNP, its absorption ability was higher which indicates that the multiple functional groups on MNP-OPP played an important role in the enhancement of the absorption ability. Characterization of MNP-OPP by FTIR, SEM, XRD, TEM and VSM also revealed the covalent binding of hydroxyl groups of MNP with the carboxyl groups of OPP, and further confirmed its physico-chemical properties favorable for metal binding. Results of the study revealed a faster kinetics and

efficiency of MNP-OPP in comparison to those of MNP and OPP and further confirmed a complexation and ion interchange mechanism to be operative in metal binding. It was discussed by the authors that at $\text{pH} > \text{pH}_{\text{pzc}}$, $\text{Fe}-\text{OH}$ and $-\text{Fe}-\text{O}-(\text{C}=\text{O})-(\text{OH})_n$ are the dominant variety in MNP and MNP-OPP respectively. Such deprotonated variety undergo electrostatic attraction for Cd^{2+} that result in the formation of metal-ligand magnetic composite complexes which caused enhanced adsorption. The elimination of textile dyes (Direct Red 23 (DR23) and Direct Red 80 (DR80)) from aqueous solutions by orange husk was examined [41].

The absorption ability was found to be 10.72 and 21.05 mg/g at initial pH 2. The results indicated that acidic pH supported the absorption of both dyes on the adsorbent. Orange peel with concentrations of 8 and 4 g/L showed absorption efficiencies of about 92 and 91% for DR23 and DR80, respectively. Maximum desorption of 97.7% for DR23 and 93% for DR80 were achieved in aqueous solution at pH 2. The potential use of stimulated carbon prepared from orange husk for the elimination of direct blue-86 (DB-86) dye from simulated wastewater [42]. Ideal pH value for dye absorption was determined as 2.0. Maximum dye was sequestered within 30 min after the beginning for every experiment. The absorption of Direct blue 86 followed a pseudosecond-order rate equation and fitted well Langmuir, Tempkin and Dubinin-Radushkevich (D-R) models better than Freundlich and Redlich-Peterson models. The maximum elimination of direct blue-86 was acquired at pH 2 as 92% for adsorbent dose of 6 g/L and 100 mg/L initial dye concentration at room temperature. The maximum absorption ability acquired from Langmuir model was 33.78 mg/g. The elimination of textile dyes from artificial textile dye effluent by stimulated carbons developed from orange husk was examined [43].

Direct Yellow 12 (DY-12) was used as the model compound due to its wide range of applications and high stability in the environment. The maximum elimination was 96% for 125 mg/L of DY-12 concentration at 5 g/L carbon concentration. The results indicated that acidic pH (1.5) supported the absorption of DY-12 on stimulated carbon developed from orange husk. The maximum absorption ability calculated from the Langmuir isotherm model was 75.76 mg/g. Stimulated carbon developed from orange husks was used for the elimination of Direct Navy Blue 106 (DNB-106) from wastewater [44]. The maximum absorption ability was 107.53 mg/g for 150 mg/L of DNB-106 concentration and 2 g/L carbon concentration. Absorption of the reactive gray BF-2R dye from an aqueous solution using orange waste as adsorbent was examined in batch mode [45]. Characterizing the orange husk using the BET method, surface area of $2.14 \text{ m}^2\text{g}^{-1}$ with a pore volume of $4.871-4 \text{ cm}^3\text{g}^{-1}$ a pore size of 9.24 Å was obtained. Experiments characterizing the chemical and physical properties of the adsorbent found that orange husk is a microporous material with a pH_{pzc} (point of zero charge) 3.9 and containing carboxylic and sulfonic groups. The greatest absorption ability was acquired using a 23 factorial design for 0.25 g of adsorbent, particle size $<0.419 \text{ mm}$ and at 300 rpm.

The absorption of naphthalene from aqueous solution onto unripe orange waste has been examined [46]. Results of the batch absorption experiment showed that equilibrium absorption was achieved in 180 min. The absorption ability of the unripe orange husk for an initial 100 mg/L of naphthalene was maximum at an ideal pH of 6, with an orange peel loading of 7.5 g. Orange peel was also utilized as low-cost adsorbent to eliminate carbofuran from aqueous solution [47]. The maximum monolayer absorption ability was found to be 84.49 mg/g at 30°C. Both Langmuir and Freundlich models fitted the absorption data quite reasonably ($R^2 > 0.98$) and the maximum absorption ability was 161.29 mg/g. Pomelo husk as biosorbent using the zinc chloride activating method was used in laboratory to test its ability of removing Pb^{2+} from wastewater [48].

The optimal stipulations for the absorption were found to be: 5.3-6.5 initial pH of the wastewater, 1.5 h of exposure duration, 10 g/L adsorbent dosage, 100 mg/L of initial Pb^{2+} concentration of wastewater at 30°C. Under the given experimental parameters, the adsorbent could eliminate more than 90% of Pb^{2+} from the wastewater. Factors affecting absorption such as initial pH, initial concentration, contact time and temperature were investigated. It was found that the highest Cu^{2+} absorption ability for PP and DPP were 19.7 mg/g and 21.1 mg/g at the following conditions: pH: 4, initial concentration: 125 mg/L, temperature: 25 °C and equilibrium time: about 60 min. Pomelo husk was also examined as adsorbent to treat the simulated dye wastewater with methylene blue [49]. The surface area and intermediate pore radius were 0.034 m²/g and 1.3×10^{-3} μm, respectively, as measured using the BET (Brauner Emmett Teller) method with nitrogen gas. Maximum absorption ability was acquired as 16 mg/g at pH 2 and 303 K solution temperature. The absorption process was observed to be reaching equilibrium after about 90 min. stimulated carbon produced from pomelo peels (PPAC) was tested for its effectiveness in the elimination of malachite green (MG) dye from aqueous solution [50]. Results of proximate analyses of PPAC showed that moisture (9%), ash (8.2%) and volatile matter (11.4%) contents were low however; the fixed carbon content (71.4%) was satisfactory. Ultimate analysis showed high percentage of elemental carbon (75.8%), low hydrogen (2.95%) and nitrogen (1.53%) contents and an insignificant value for Sulphur (0.32%). The surface area of PPAC was found to be 1357.21 m²/g. The intermediate pore diameter of the prepared sample was found to be 2.72 nm. Dye elimination was pH dependent, resulting in 95.06% elimination at pH 8.0.

Quantum chemical studies suggested that the cationic MG dye possessed minimal molecular size at planar geometry coupled with high electrostatic interaction thereby, enhancing the absorption at high pH. Langmuir isotherm fitted the absorption data reasonably well with maximum monolayer absorption ability of 178.43 mg/g. Regeneration efficiency of spent PPAC was studied using 0.2 M HCl, and the efficiency was found to be in the range of 92.71–96.35% after four cycles. Besides these, several other researchers also examined pomelo husks as adsorbents for the elimination of varied aquatic

pollutants [51]. Natural grapefruit husk (GFP) exhibit good efficacy to adsorb uranium(VI) [52]. Through the fixed bed column technique, absorption characteristics of uranium(VI) was observed at varied flowrate, bed depth, influent uranium(VI) concentration and particle size of adsorbent. The results showed that absorption reached saturation faster with increasing the flow rate and influent uranium(VI) concentration. The data were fitted to the Thomas model, the Yan model, the Clark model and the mass transfer model by nonlinear regressive analysis. When the flow rate was 8.0 mL/min and the influent concentration of uranium(VI) was 90 mg/L, the maximum absorption quantity reached 104.1 mg/g according to the Thomas model. The bed depth service time model was applied to predict the service times with other flow rate and initial concentration.

The theoretical penetration curve was compared with experimental penetration curve profile in the dynamic process. The results showed that the Yan model was better for the description of penetration curves at the experimental stipulations than the Thomas and the Clark models. The saturated column was renewed by 0.05 mol/L HCl solution and GFP could be reused in uranium(VI) removal. The biosorption of cadmium and nickel onto grapefruit husk from aqueous solution has been examined using batch technique [53]. The maximum uptakes of Cd(II) and Ni(II) by grapefruit husk were found to be 42.09 and 46.13 mg/g, respectively. Authors suggested that the main sorption mechanism was ion interchange due to the release of cations and protons from the biosorbent during sorption of Cd(II) and Ni(II) ions. FTIR analysis demonstrated that carboxyl and hydroxyl groups were involved in the biosorption of metal ions. The recovery of the Cd(II) and Ni(II) from grapefruit husk was found to be more than 97% using 0.1 M HCl. The absorption potential of lemon waste was examined as an adsorbent for the elimination of two dyes from aqueous solutions [54].

The absorption capacities of lemon waste adsorbent for dyes were found to be 50.3 and 34.5 mg/g for MO and CR, respectively. Batch absorption studies were conducted to eliminate cutting oil from wastewater using stimulated lemon husks [55]. The effect of different important parameters, namely, pH, dose of adsorbent, contact time, mixing speed, and initial oil concentration, and their ideal stipulations for maximum sorption efficiency were examined and results indicated that adsorbent dosage of 5g/L, contact time of 70 min, mixing rate of 45–50 revolutions/min, and pH of 2 provided maximum oil elimination efficiency in this study. The feasibility of lemon husk waste was examined for the elimination of cobalt ions from aqueous solutions [56]. The maximum absorption ability of lemon husk adsorbent for cobalt elimination was ca. 22 mg/g. elimination of methylene blue (MB) from aqueous solution using orange husk biosorbent was examined [57]. The maximum absorption capacities of the orange husk were 246.8 ± 10.6 and 370.3 ± 31.0 mg/g at pH 7 and pH 10, respectively. The binding sites were identified to be primary carboxyl groups present in the orange waste. The main mechanism of MB absorption was considered to be electrostatic interaction by the researchers.

The biomass Citrus limetta fruit husks were examined for its potential for Pb^{2+} ions [58]. Cold alkali remediation resulted in increased absorption of Pb^{2+} due to de-esterification of the galacturonic acid present in the biomass. Carboxylate groups in the biomass played an important role in Pb^{2+} binding as demonstrated by selective blocking experiments, as well as by FT-IR spectroscopy. A higher absorption of metal ions was found with increasing pH, increasing initial metal ion concentration, and lessening biomass concentration. Ion interchange was identified to be the dominant mechanism. Pb^{2+} binds with the carboxylic groups of galacturonic acid chain, forming a stable gel. The Langmuir sorption ability of 630 mg/g was reported which was found much higher than the efficiency of most biosorbents and comparable to those of synthetic ion-exchange resins. The absorption of Pb^{2+} by processed orange husks was also examined by Schiewer and Balaría [59].

Potentiometric titrations showed a significantly higher negative surface charge of protonated husks compared to original husks, with acidic groups around pH 4, 6, and 10. The highest measured Pb^{2+} absorption by orange husks was found to be 1.93 mmol/g (approximately 400 mg/g), however, no plateau value was achieved in the study. The maximum absorption ability according to the Langmuir model was 3.18 mmol/g (658 mg/g), which was reported very high for other biosorbents and similar to some ion interchange resins. Besides these, several other researchers also examined citrus husks or lemon husks as adsorbents for varied aquatic Contaminants elimination [60].

Research studies on banana peels shows capability to adsorb metal ions including lead, copper, zinc and nickel [61, 62]. The binding of metal ions onto banana peels was found to be pH dependent and the uptake was higher for acidic medium; with the optimal sorption occurring at pH 4. In a banana peel the biochemical components include cellulose, hemicelluloses, chlorophyll pigments, and pectin substances, which contain galacturonic acid, arabinose, galactose, and rhamnose. Galacturonic acids cause the pectin to strongly bind to the metal ions because of the carboxyl functions of the sugar. Cellulose also allows heavy metal ions to bind [63]. Banana peels also contain amine, hydroxyl and carboxylic groups. These structural groups are responsible for the peels' ability to bind the toxic metals and remove them from the water. Maximum absorption ability of banana husks from Langmuir isotherm indicated that 1 g of banana husks can adsorb 5.71 mg of cadmium and 2.18 mg of lead. Untreated banana peels (UTBPs), alkali-hydrolyzed banana peels (ALBPs), acid-hydrolyzed banana peels (AcBPs), and bleached banana peels (BBPs) were used as adsorbents separately for the elimination of Cr(VI) and Mn(II) from aqueous solution during batch experiments [64]. The maximum elimination capacities for Cr(VI) were UTBP (45%), ALBP (87%), AcBP (67%) and BBP (40%). While for Mn(II), the maximum elimination capacities of these adsorbents were UTBP (51%), ALBP (90%), AcBP (74%) and BBP (67%) at ideal conditions. The maximum elimination of Cr(VI) and Mn(II) was acquired

at initial concentration of 3 mg/L, adsorbent dose of 4 g/L, pH 6, and contact time of 60 min. It was noted that the metal ions elimination ability of these adsorbents was $\text{ALBP} > \text{AcBP} > \text{UTBP} > \text{BBP}$, which indicated that chemical treatment of banana peels promote the biosorption of metal ions. The absorption of metals (Cu^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Pb^{2+}) from synthetic solutions using the acid, alkali, and water-treated banana peels was examined [65].

The absorption ability was found to be 7.97 (Pb^{2+}), 6.88 (Ni^{2+}), 5.80 (Zn^{2+}), 4.75 (Cu^{2+}), and 2.55 mg/g (Co^{2+}) using banana peel. The potential application of banana peel as a biosorbent for removing organic compounds such as phenolic from olive mill wastewaters was examined [65]. The banana peel showed a high absorption ability of phenolic compounds (689 mg/g). The absorption process was very fast, and it reached equilibrium in 3 h of contact time. The equilibrium solid-phase concentration of phenols decreased with increasing adsorbent (banana peel) concentration was mainly attributed to the unsaturation of the absorption sites through the absorption process. Desorption experiments showed chemisorptive interactions between the natural phenolic and the absorption sites on the banana peel. Remediation of a basic dye, methylene blue, from an aqueous solution was examined by biosorption on banana husks waste [66]. The biosorbent was chemically modified with caustic soda (NaOH). The maximum values of absorption capacities for activated banana peel (ABP) were 19.671 mg/g and 18.647 mg/g for natural banana husk (NBP) at pH 4–8, 20°C. The adsorptive behavior of Acid Blue 25 (AB25) dye on the banana peel is studied [67]. Analysis of the acid-base properties of the biomass provided the number of weak acid groups, that was found to be 0.288 (7) mmol/g for modified banana husk in 0.1 M KNO_3 . An adsorption ability value of 0.215 (13) mmol/g was acquired by fitting the batch experiments data to sorption isotherms. The application of banana waste for the remediation of heavy metals (Pb, Zn and Cr) was examined [68].

The adsorbent stimulated with 0.5M H_2SO_4 showed the highest percentage removal of chromium ion (88.9%) at pH 6. It was found that particle size had no effect on the uptake of zinc ion and it was also reported that the elimination efficiency of lead and chromium ion decreased with increase in contact time and particle size. Authors also reported that untreated banana husk waste increased the biochemical oxygen demand (BOD) and chemical oxygen demand (COD) values of wastewater. Atrazine elimination from water by treated banana waste was examined. Batch experiments demonstrated that 15 g/L adsorbent dosage removed 90-99% of atrazine from 1-150 ppm aqueous solutions. The elimination was both pH and temperature dependent with the most atrazine removed between pH 7 and 8.2 and increased with increasing temperature. Equilibrium data fitted well to the Langmuir and Redlich-Peterson models with a maximum absorption ability of 14 mg/g. The feasibility of using banana peel for removal of the pesticides atrazine and ametryne from river and treated waters has been studied.

The stipulations for removal of these pesticides in a laboratory scale were optimized as sample volume = 50 mL,

banana mass = 3.0 g, stirring time = 40min, and no pH adjustment necessary. The uptake potential of ametryne by the banana husk was found to be high as the $K_F(\text{sor})$ (Freundlich parameter) value was estimated as 54.1 $\mu\text{g/g}$ which corresponds to 75.3% of the applied ametryne amount. A moderate sorption potential was estimated for atrazine [$K_F(\text{sor}) = 35.8 \mu\text{g/g}$], corresponding to 59.8% of the applied atrazine amount. Moreover, several other researchers also reported the capability of banana waste as adsorbents for varied aquatic pollutant removal [69]. The ability of activated carbon from cassava husks to remediate Cu(II) and Pb(II) from hospital wastewater was illustrated [70].

The study showed that pH 8 was the best for the sorption of both metal ions onto the biosorbent. The time-dependent experiments for the metal ions showed that the binding of the metal ions to the biomass was speedy and occurred within 20–120 min. Sorption efficiency was found to increase with a rise in adsorbent dosage and it increased from 12 to 73% for Pb(II) and 26 to 79% for Cu(II) when the adsorbent dose increased from 2 to 12 g. An increase in temperature led to an increase in sorption for both metal ions. The Langmuir model showed that the biomass has a higher sorption ability for Cu(II) than Pb(II) (5.80 mg/g for Pb(II) and 8.00 mg/g for Cu(II)). The adsorption of methyl red, an azo dye from aqueous solution onto NaOH-activated cassava husks carbon in a fixed-bed column was illustrated [71]. Ideal adsorption ability of 206.08 mg/g was acquired at carbon bed height of 20cm, inlet concentration of 200 mg/L and flow rate of 13.3 mL/min. The maximum adsorption of 78.62% was acquired for inlet concentration of 50 mg/L, carbon bed height of 30 cm and flow rate of 13.3 mL/min. The ability of cassava husk to eliminate Cu(II) from aqueous solution was also evaluated and a maximum adsorption ability of 41.77 mg/g was reported [72]. The feasibility of cassava husk waste for Ni sorption was also evaluated [73]. Sips model demonstrated the best fitting with the maximum adsorption ability for Ni(II) ions as 57 mg/g (0.971 mmol/g) at pH 4.5.

The capability of using jackfruit peel (JFP) for the absorption of methylene blue was studied [74]. Batch absorption studies were conducted to evaluate the effects of contact time, initial concentration (35–400 mg/L), pH (2–11), and adsorbent dose (0.05–1.20 g) on the elimination of dye at temperature of 30°C. The experimental data fitted well with the type 2 Langmuir model with a maximum absorption ability of 285.71 mg/g. The effect of jackfruit husk waste for remediate Rhodamine dye from aqueous solution was studied [75]. The effect of absorption isotherm was examined by carrying out a series of isotherm at varied adsorbent dosages (1.0, 2.0, 3.0 g/L), temperatures (30, 40 and 60°C) and pH (4.95, 8.14, 9.74), respectively. The monolayer absorption ability was determined to be 4.361 to 1.98 mg/g. The effectiveness of an adsorbent prepared from jackfruit husk for the elimination of phenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol from aqueous solutions was examined [76].

It was found that after mercerization remediation of husk, the proportion of C and H were decreased. The absorption

equilibrium was reached in 5 h. The order of elimination was found to be 2,4-dichlorophenol > 4-chlorophenol > 2-chlorophenol > phenol. The maximum sorption capacities for phenol, 2-chlorophenol, 4-chlorophenol, and 2,4-dichlorophenol were found to be 144.9 mg/g, 243.9 mg/g, 277.7 mg/g, and 400.0 mg/g, respectively. The elimination of phenols was found to be most effective at lower pH. The pomegranate waste was also tested for Cu(II), Ni(II), Cd(II), Zn(II) and Cr(VI) ions [77]. The maximum adsorption was observed for Cu(II) ions, followed by Zn(II), Cd(II), Ni(II) and Cr(VI) ions. Attempts were made using batch and column methods to desorb Cu(II), Ni(II), Zn(II), Cd(II) and Cr(VI) ions from synthetic wastewater as well as from wastewater derived from electroplating activities. The penetration capacities of Cu(II), Ni(II), Zn(II), Cd(II) and Cr(VI) ions were 6, 2, 2, 2 and 0 mg/g, respectively, when a mixture of these metal ions was treated. The adsorbent was utilized to recover Cr(VI) ions from electroplating wastewater. The use of stimulated carbon prepared from pomegranate waste for the elimination of direct blue 106 dye from aqueous solution was examined [78]. Remediation of dye was pH dependent and the maximum uptake was achieved at pH 2. The optimum absorption was achieved in 120 min. The absorption potential of pomegranate waste was studied for the removal of 2,4-dichlorophenol (2,4-DCP) from aqueous solutions [79]. The absorption ability of pomegranate waste adsorbent for 2,4-DCP was found to be 65.7 mg/g. Pomegranate waste carbon was also studied for its capability to adsorb iron(II) ions from solutions [80]. The high adsorption capacity of pomegranate waste activated carbon for iron(II) was found to be 18.52 mg/g (calculated by Langmuir model) at pH 6.0 and 1 g L⁻¹ of biosorbent concentration at 29°C. The viability of garlic peel (GP) to eliminate Pb²⁺, Cu²⁺ and Ni²⁺ was evaluated [81].

The results showed that the absorption process could reach equilibrium within 20min. GP had remarkable higher absorption affinity for Pb²⁺ than Cu²⁺ and Ni²⁺ with the maximum absorption ability of 209mg/g. The absorption efficiency and adsorption ability of one metal ion were lessened by the presence of the other metal ion. The absorption mechanism was supposed to be ion interchange between Ca²⁺ of GP with heavy metal ions in the solution. Native garlic husk and mercerized garlic husk as adsorbents for the elimination of Pb²⁺ has been examined [82]. An adsorbent prepared from Citrus limetta husk was used to study its sorption potential on removing Brilliant green dye [83]. A maximum dye uptake of 95% was achieved with an initial concentration of 10mg/L. Zirconium loaded apple husks were used to extract anions such as phosphate, arsenate, arsenite, and chromate ions from aqueous solutions [84]. Zr treated apple husks showed efficient absorption toward AsO₄³⁻ (15.64 mg/g), AsO₄³⁻ (15.68 mg/g), Cr₂O₇²⁻ (25.28mg/g), and PO₄³⁻ (20.35 mg/g) anions.

The absorption and desorption studies showed the adsorption mechanism involved electrostatic interactions. Arsenate and chromate anions were strongly adsorbed at the pH range from 2 to 6, while arsenite was extracted efficiently

between pH 9 and 10. The absorption of Methylene Blue (MB) and Acid Orange 7 (AO7) dye onto *Ananas Comosus*. Mixed Husks and Leaves (ACMPL) was examined [85]. Highest percentage elimination for MB was showed at pH 9, which was 95.81%. Meanwhile for AO7, the highest percentage elimination was 31.06% at pH 3. The percentage elimination of MB had reached the equilibrium at dosage 0.5 g while AO7 kept increasing with the increment of adsorbent dosage. The percentage removal of MB and AO7 had increased until 2.5 h which was from 72.5% to 86.93% and 19.441% to 36.89% respectively, and retain equilibrium in 3 h. The absorption ability of stimulated carbon prepared from guava fruit husk waste has been examined for congo dye [86]. The activation process was carried out under microwave radiations in the presence of KOH. The maximum absorption ability for congo dye was found to be 61.12 and 120.62 mg/g for inactivated and KOH⁺ microwave heated guava fruit husk. The utilization of ash gourd (defatted) husk in biosorption of chromium was reported [87]. The BET surface area of powder was found to be 0.4854 m²/g. In equilibrium studies at pH 1, more than 91% Cr(VI) was adsorbed on ash gourd husk powder at an adsorbent dosage of 6 g/L for 125 mg/L solution.

The sorption ability of husk for Cr(VI) in batch studies was 18.7 mg/g. FTIR spectroscopy of samples before and after absorption revealed the presence of carboxyl functional group, which played an important role in absorption of Cr(VI). The processing of 1000 kg of ash gourd generates husk was capable of adsorbing as high as 261.8 g of Cr(VI). Breadnut skin, in both its unmodified (KS) and base-modified (BM-KS) synthesized, was examined for its potential use as a low-cost adsorbent for the elimination of malachite green (MG) [88]. The absorption ability was greatly enhanced when breadnut skin was chemically modified with NaOH, leading to an absorption ability of 353.0 mg/g. Regeneration experiments on BM-KS indicated that its absorption ability was still maintained at >90% even after five cycles. Husk of breadnut, *Artocarpus camansi*, was also examined for the elimination of methylene blue (MB) [89]. A maximum biosorption ability of 409 mg/g was reported for MB by husk of breadnut.

Removal of ultramarine blue dye from aqueous solution using yam husks waste was examined by Owamah et al. [90]. Maximum absorption was found to happen at pH 10. Maximum absorption ability was acquired as 0.940 mg/g. The absorption of malachite green (MG) dye onto rambutan peel-based activated carbon (RPAC) was examined by Ahmad and Alrozi [91]. Solution pH >8 was proved to be more favorable for absorption of MG on the RPAC. Boyd plot revealed that the adsorption of MG on RPAC was controlled by film diffusion. The same researchers also used the rambutan peel based activated carbon (RPAC) for Remazol Brilliant Blue R elimination [92]. The ideal conditions for RPAC preparation were acquired by using activation temperature of 789 °C, activation time of 1.8 h and impregnation ratio of 3.5, which resulted in 78.38% of RBBR elimination and 18.02% of RPAC yield. Rambutan (*Nephelium lappaceum*) peel was also used as the precursor for preparation of activated carbon by chemical helped KOH

activation and tested for acid yellow 17 dye absorption [93]. The maximum monolayer absorption ability of dye was found to be 215.05 mg/g. Activated carbons were synthesized from durian husk and used for the elimination of lead(II) ions from water [94]. The activated carbons were produced with physical activation method using CO₂ as the activating agent at 900°C. Prior to the activation process, durian husk was carbonized under either nitrogen atmospheric or vacuum pyrolysis. The results showed that the stimulated carbon formed under vacuum pyrolysis had greater BET surface area, pore volume and lead(II) absorption ability than that formed under nitrogen atmospheric pyrolysis. A low-cost stimulated carbon was developed from kiwi husk for removing Pb(II) from aqueous solution. The adsorbent demonstrated remarkable characteristics such as high surface area (306.18 m²g⁻¹) and large total pore volume (0.4810 cm³g⁻¹).

It was found that the ideal pH for removing Pb(II) was 6. The maximum absorption ability of Pb(II) adsorbed by kiwi husk-based stimulate carbon was 158.82 µg.g⁻¹. Durian peel (DP) was examined for its ability to eliminate Basic blue 3 (BB3) from aqueous solutions [95]. The maximum absorption ability of DP for BB3 was found to be 49.50 mg/g. *Raphanussativus* peels (RSP) biomass for the adsorptive elimination of cadmium(II) has been examined [96].

The maximum absorption ability was determined to be 19.82 mg/g under the ideal conditions. Namasivayam and Periasamy [97], converted peanut hull into an adsorbent peanut hull carbon (PHC) by treating it with concentrated sulfuric acid, then carbonizing in air atmosphere and further treating with 1% sodium bicarbonate overnight. The treated material was used as an adsorbent for the removal of Hg (II) from aqueous solutions. The adsorption conformed to both Freundlich and Langmuir isotherms. The authors observed much superior adsorption capacity (109.89 mgg⁻¹) for the bicarbonate treated peanut hull compared to a commercial granular activated carbon (12.38 mgg⁻¹), which was suggested to be due to higher porosity and the moderate ion exchange capacity of the bicarbonate treated peanut hull compared to the activated carbon. The same adsorbent (PHC) was also used for Cd (II) adsorption, and the authors [98] found that the process conformed better to the Freundlich rather than the Langmuir model. However, in the case of Pb (II) adsorption [99] on PHC, the process was found to obey the Langmuir model. In all the cases (i.e., Hg (II), Cd (II), and Pb (II)), the adsorption kinetics was found to be up to five times faster than that found with a commercial granular activated carbon, and the adsorption capacity was 9 to 32 times higher. Peanut shell has also been used by Chamrathy et al., [100] who prepared adsorbents by heat treatment in the presence of phosphoric or citric acid and used it for the adsorption of Cd²⁺, Cu²⁺, Ni²⁺, Pb²⁺, and Zn²⁺. Their investigations showed that phosphoric acid-modified shells adsorbed metal ions in larger amounts compared to citric acid modified shells. Besides them, the potential of peanut hull pellets to capture metal ions Cu²⁺, Cd²⁺, Zn²⁺, and Pb²⁺ from wastewater and their performance comparison to that of raw peanut hulls and a commercial grade ion-exchange resin has been carried out by Brown et al. [101]

as well. A simple cost analysis done by the workers has shown that the peanut hulls and hull pellets outperform the resin in terms of gram metal removed per media cost. *Hazelnut shells*. Batch and column adsorption studies of methylene blue and acid blue 25 onto ground hazelnut shells and sawdust of four wood species—namely, walnut, cherry, oak, and pitch-pine were carried out by Ferrero [102] in order to explore the potential use of these materials as low cost adsorbents for dye removal from dye house effluents. The adsorption kinetics with all adsorbents was found to fit a second-order rate equation better than Lagergren's first-order model.

Further, the equilibrium data agreed well with Langmuir's model, and higher adsorption capacity (given for mean particle diameter 125 μm) was observed for hazelnut shells in comparison to wood sawdust for both dyes. The adsorption capacity for methylene blue was even higher (due to the presence of polar functional groups) than that for activated carbon from the same material due to the fact that thermal activation develops a highly microporous structure, which is inaccessible to large dye molecules and conversely destroys the functional groups on the surface that are involved in the adsorption mechanism. Almond shell, olive stones, peach stones, apricot stone shells, pinhao. Almondshell, olive stones, and peach stones were studied as adsorbents after processing for the removal of Zn^{2+} , Cd^{2+} , and Cu^{2+} from aqueous solutions by Ferro-Garcia et al., [103] which were found to have appreciable surface areas of 876, 1103, and 1316 m^2g^{-1} , respectively. Apricot stone shells have been studied using chemical treatment and low activation by Daifullah and Girgis [104] for the removal of substituted phenols, who suggested that the adsorption of phenols on these adsorbents was inversely proportional to their solubility. Wastes of *Araucaria angustifolia* [105] (also named *pinhao*) in its natural state and loaded with Congo red were tested as low-cost adsorbents for Cu (II) removal from aqueous solutions. Optimization was carried out in order to reduce the total number of experiments and to achieve the best conditions for the batch adsorption procedure. It was found that the *pinhao* wastes with Congo red increased the amount of Cu (II) uptake by more than two times using the Langmuir maximum adsorption or more than three times using the Freundlich maximum capacity.

It was suggested that the presence of amino and azo groups on congo red, which is loaded on *pinhao* wastes, should be responsible for the enhancement in adsorption capacity. *Sunflower stalks, maize cob*. The feasibility of utilizing sunflower stalks, a renewable agricultural waste available at low cost, was explored by Sun and Shi. [106]. The source material was sieved, and adsorption of Cu^{2+} , Zn^{2+} , Cd^{2+} and Cr^{3+} was studied. The adsorption was found to be physical with an adsorption capacity of 29.3, 30.73, 42.18, and 25.07 mgg^{-1} for Cu^{2+} , Zn^{2+} , Cd^{2+} , and Cr^{3+} , respectively. Sunflower stalks were also studied as adsorbents for basic and direct dyes in aqueous solutions with equilibrium isotherms and kinetic adsorptions. The authors observed high adsorption capacities for basic dyes as compared to direct dyes. The authors suggested that because sunflower stalks consist of cellulose, it is the polyol structure of cellulose-based materials that has

relatively strong chemical adsorption of cations such as metal ions and organic bases as well as physical adsorption of other materials such as acidic and anionic compounds.

Also, the greater affinities of basic dyes for sunflower stalks than that of anionic dyes can be attributed to the cellulosic structure of the materials. The coulombic forces between dye species and negatively charged cellulose in water are the major interactions that affect the adsorption of dyes on the materials. El-Geundi [107] studied maizecob, an agricultural waste, without any pretreatment for the removal of two basic dyes (astrazone blue and maxilon red) and two acid dyes (telon blue and erinoyl red). The agricultural waste was found to have high adsorption capacities of 160 and 94.5 mgg^{-1} for astrozone blue and maxilonred and low capacities of 47.7 and 41.4 mgg^{-1} for erinoyl red and telon blue, respectively. Lignin is the second most abundant natural raw material and nature's most abundant aromatic (phenolic) polymer, and is generally obtained from black liquor, a waste discharged from paper mills in large quantities. It has been used in its raw state as well as modified for removal of contaminants by researchers.

Acemiolu et al. [108] used organosolv lignin as sorbent for the removal of copper (II). It was suggested that organosolv lignin, which is produced through the delignification of wood and other lignocellulosics in organic solvents such as methanol, butanol, and ethanol, has been found to be quite similar to natural lignin but more attractive because it does not contain sulfur. However, the adsorption of Cu (II) was found to increase with concentration and pH and decrease with temperature. Cu (II) was studied by Sciban and Klasnja [109] and Merdy et al. [110].

The removal of the toxic metals Pb (II) and Cd (II) onto modified lignin from beech and poplar woods by alkali glycerol delignification was studied by Demirbas, [111] who found the adsorption process to be endothermic in nature and followed the Langmuir model. The maximum adsorption capacities of 8.2–9.0 and 6.7–7.5 mgg^{-1} of the modified lignin for Pb (II) and Cd (II), respectively, were reported. Kraft lignin was studied for removal of Cu (II) and Cd (II) by Mohan et al., [112] and adsorption capacities of 87.05 and 137.14 mgg^{-1} were reported for Cu (II) and Cd (II), respectively. In order to evaluate the potential of a beech saw dust as low-cost adsorbent, the removal of methylene blue and basic red 22 was tested by Batzias and Sidiras. [113].

The authors also tested the potential of the adsorbent by treating it with CaCl_2 and using mild acid hydrolysis, and found it to increase the adsorption capacity. In addition, the simulation studies for effect of pH were also carried out by Batzias and Sidiras. [113]. The authors determined the point of zero charge p. z. c. (5.2) of the sawdust and reported that the increase of the pH improve the adsorption behavior. The lower adsorption of methylene blue at acidic pH was suggested to be due to the presence of excess H^+ ions that compete with the dye cation for adsorption sites. With the increase of the pH of the system, the number of positively charged sites decreases while the number of the negatively charged sites increases. It was also suggested that the negatively charged sites favor the

removal of dye (cationic like methylene blue) due to electrostatic attraction. The efficiency of the coir pith has been investigated.

Agricultural wastes have been investigated as adsorbents for metals and dyes by Namasivayam et al., [114] respectively. Corn cob as a low-cost adsorbent has also been used for making microporous activated carbon using zinc chloride by Tsai et al. [115] Wool carbonizing waste, rubber seed coat. Wool carbonizing waste, obtained as a result of processing of wool, was investigated by Perineau et al. [116] for the adsorption of dyes. They suggested that the surface properties of the material are such that it tends to adsorb solutes of ionic nature. They further observed that removal of basic dyes is 6–10 times higher than that of acid dyes. Yamada et al. [117] studied phosphate liberation from sediment by adsorption. They reported that soft granulated slag adsorbs phosphate more than hard granulated slag and explain it on the basis of porosity of the adsorbent. Dimitrova [118] investigated the elimination of Cu^{2+} , Ni^{2+} , and Zn^{2+} ions from aqueous solution using un granulated blast furnace slag. The adsorption studies were carried out in the concentration range 1×10^{-4} – 1×10^{-3} M, and it was suggested that the slag alkalizing activity creates conditions for adsorption through the formation of hydroxo complexes and colloidal particles of silicic acid.

Johansson and Gustafsson [119] used slag and opoka for increasing abiotic sorption efficiency of an on-site water treatment system. These materials were used to retain phosphorous in the plant, and they reported through sorption experiments that some slags are efficient retainers for phosphorous. Blast furnace slag has been used by others workers too [120] In addition to blast furnace slag, another waste material generated in steel plants is blast furnace sludge, which is obtained while removing dust load from the exhaust flue gas of the blast furnace through water scrubbers. This blast furnace sludge was used by Jallan and Pandey [121] as an adsorbent without any treatment for the removal of toxic Pb^{2+} , Ni^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , and CN^- ions. They reported that sludge has a good adsorptive property for metal ions as well as cyanide. In case of Zn^{2+} adsorption, however, the high adsorption was poor (9 mg g^{-1}). The sorption of some heavy metals on sludge was also studied by L'opez-Delgado et al., [122] who illustrated that metal ions are adsorbed in the order of $\text{Pb}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$.

The process was found to be endothermic and the adsorption data fitted both Freundlich and Langmuir isotherms. Blast furnace sludge has also been utilized for the removal of dyes and phenols by Jain et al. [123] Bagasse, bagasse pith, bagasse fly ash. Raw bagasse is a waste from sugar mills and has been used as a low-cost adsorbent for elimination of chromium and nickel from aqueous solution by Rao et al., [124] who reported the effect of hydrogen ion concentration, contact time, sorbent dose, initial concentrations of adsorptive and adsorbent and particle size in batch experiments. The efficiency of the material for the removal of Cr (VI) at pH 6 and Ni (II) at pH 8, with a sorbate concentration 100 mg/L, contact time 90 min, adsorbent particle size 75 μm , and adsorbent dose 3.5 g/L, was found to

be 91 and 85.6%, respectively. The efficiency of bagasse was suggested to be comparable to costlier conventional powdered simulated carbon.

Further, bagasse pith from the sugarcane industry has been studied by McKay et al. [125] without any pretreatment for the removal of two basic dyes, basic blue 69 and basic red 22, and two acidic dyes, acid blue 25 and acid red 114, from aqueous solutions. High adsorptive efficiency was observed for the adsorption of the basic dyes, 158 mg g^{-1} for basic blue 69 and 77 mg g^{-1} for basic red 22, while lower capacities of 23 mg g^{-1} and 22 mg g^{-1} were observed for acid red 114 and acid blue 25, respectively. The same material was also studied by Al-Duri et al. [126] for developing a mass transfer model, based on external mass transport and macropore and micropore diffusion to predict concentration versus time decay plots of adsorption.

Srivastava et al. [127] converted bagasse flyash into a low-cost adsorbent for the removal of substituted phenols. The authors compared the uptake of trinitrophenol on the bagasse flyash with other commercially available adsorbents. It was suggested that the developed bagasse flyash adsorbent is considerably effective and cheap. The removal of dinitrophenol has also been observed, and the cost estimation of bagasse flyash indicated that the waste bagasse flyash is available for 60 Indian Rs ton^{-1} (1.3 US \$ ton^{-1}) and considering the cost of transport, chemicals, and electrical energy used in the process, the finished product would cost approximately 400 Indian Rs ton^{-1} (8.9 US \$ ton^{-1}). The cost analysis reported that the adsorbent may be a good replacement for commercially available carbon due to its comparable efficiency and a significantly lower cost. The results showed that 86% of dinitrophenol can be removed using 10 g L^{-1} of activated bagasse flyash. Bagasse flyash has also been used for the removal of phenol and *p*-nitrophenol from wastewater obtained from a coal gasification plant by Gupta et al. [128] Batch studies showed that 95% of phenol and 100% of *p*-nitrophenol can be removed by using 10 g dm^{-3} of adsorbent at pH 4.0. It was found that the adsorption capacity KF is less for the phenol-bagasse flyash system than that for the *p*-nitrophenol-bagasse flyash system.

The Langmuir constant Q_0 decreases with an increase in temperature, thereby indicating the process to be exothermic in nature. Furthermore, studies were also performed to assess the practical utility of the adsorbent column. Desorption of the materials adsorbed was tried with a number of eluting agents and almost complete desorption (98%) of phenol could be achieved with only 8% NaOH. Regeneration of the spent column was carried out with 1M HNO_3 . A sample of actual wastewater from a coal gasification plant having phenols (2800 mg dm^{-3}) was successfully treated on the columns of this adsorbent material. Almost complete removal of phenol from 50 cm^3 of wastewater at pH 4.0 was possible with the column of bagasse flyash. In addition, Gupta et al. [128] used bagasse flyash for the removal of the pesticides lindane and malathion from wastewater as well. The authors reported a maximum uptake of 97–98% at pH 6 and a dose of 5 g/L, the adsorption was suggested to be exothermic in nature. Shale oil

ash, obtained after the combustion of shale oil was used as adsorbent by Al-Qodah [129] for dyes. The author has reported that the material, which is obtained after a high-temperature process, possesses good porosity and has good adsorptive behavior for contaminant.

Red mud is a waste from the aluminum industry and has also been indicated as an adsorbent by Shiao and Akashi. [130] The mud was modified with acid and stimulated at various temperatures, and its capacity was found to be equivalent to that of alumina. Red mud treated with seawater has been used as an adsorbent for arsenate removal from water by Genc, et al. [131] The adsorption was found to follow the Langmuir model and increased with decreasing pH, higher adsorbent dosages, and lower initial arsenate concentrations. Furthermore, the red mud has also been used for the removal of fluoride, phenol, nitrate, and congo red. Straw and used rubber tires were investigated by Streat et al. [132] for the sorption of phenol and p-chlorophenol from water. The source material was carbonized in a tube furnace in a stream of oxygen free nitrogen and followed by activation using a stream of moisture-laden nitrogen. Pseudo equilibrium sorption of phenol and p-chlorophenol obeyed a Freundlich type adsorption isotherm. Waste tire rubber was also used by San Miguel et al. [133] for the adsorption of organic compounds viz. phenol, methylene blue, and textile dyes. Fertilizer industry waste. A similar carbonaceous adsorbent was investigated by Jain et al., [134] who utilized it for the removal of dyes and phenols. The authors compared the potentials of the carbonaceous adsorbent with blast furnace slag, dust, and sludge (steel industry waste) and found the carbonaceous adsorbent to be best among them. Further, a comparison of the carbonaceous adsorbent with an activated carbon showed it to be 45% efficient as activated carbon. Carbonaceous adsorbent has also been used for the elimination of pesticides by Gupta et al. [128]. Fly ash. Fly ash is a by-product material that is produced in huge amount in thermal power plants based on coal firing.

The availability of fly ash is so high that at many places its disposal is a problem. As such, a number of workers have attempted to use it as an adsorbent in pollution control. Panday et al. [135] used flyash without any pretreatment for the removal of Cu^{2+} and found that the adsorption data conform to the Langmuir adsorption. The suitability of fly ash for the removal of phenol and chlorophenols was also investigated by Haribabu et al. [136]. They found adsorption to be endothermic and a first-order process. Fly ash has also been used by Viraraghavan and Ramakrishna [137] to remove both cationic and anionic dyes. They reported that the dye adsorption process on fly ash is of first order, and the adsorption data follow both Langmuir and Freundlich isotherms.

The results of all these studies on fly ash have shown that the adsorption capacity of fly ash is poor and, therefore, its efficiency in comparison to activated carbon is low. The fly ash has also been used in conjunction with other materials. In a separate study, two flyashes from different power plants fueled with different brown coals were tested as potential

low-cost sorbents for the removal of synthetic dyes (basic as well as acidic) from waters by Janos et al. [138].

The adsorption removal was determined from the parameters of adsorption isotherms and was found to be in the range of 10^{-1} – 10^{-3} mmol g^{-1} and did not differ significantly for basic and acid dyes. The adsorption was described well by the multi-site Langmuir isotherm. Factors affecting sorption, such as pH, the presence of organic solvents, inorganic salts, and surfactants, were also investigated. The authors found that the sorption of basic dyes increased at high pH values, whereas the opposite was found for acid dyes. The dye sorption decreased in the presence of organic solvents (methanol, acetone), whereas inorganic salts exhibited only a minor effect on the dye sorption. The presence of oppositely charged surfactants showed a pronounced effect on the dye sorption and low concentrations of the surfactant-enhanced sorption, whereas high concentrations solubilized the dyes and kept them in solution. Further, the authors suggested that the coal fly ashes can be used for the sorption of both basic as well as acid dyes from aqueous solutions without any expensive pre-treatment. Waste paper. Waste newsprint paper has also been put to use for preparing alternative adsorbents.

Shimada et al. [139] used newspaper as raw material for the production of activated carbon. Waste newsprint paper was mixed with 8% phenol resin, and the material was heated at 150°C for 10 min and was further carbonized at 800°C for 2 h under nitrogen gas followed by the activation at 900°C for 1 h under CO_2 atmosphere to get activated carbon. The activated carbon so produced possessed good surface area ($1000 \text{ m}^2 \text{ g}^{-1}$) and the yield was 40%. In view of its high surface area, this product functioned as a good adsorbent, as evidenced by high iodine (1310 mg g^{-1}) and methylene blue number (326 mg g^{-1}). Sewage sludge. Sewage sludge with additive coconut husk has been used by Tay et al. [140] for preparation of activated carbons using ZnCl_2 activation. It was suggested that low concentration of ZnCl_2 tends to improve microporosity, and 5 M ZnCl_2 was found to give the best activated sample with $867.61 \text{ m}^2 \text{ g}^{-1}$ surface area with 57.99% phenol removal capacity.

Sewage sludge has also been used to prepare carbonaceous materials using chemical activation by Rio et al. [141] Carbonaceous sorbents so developed from sludge were used to remove copper ion, phenol, and dyes (acid red 18 and basic violet 4) from aqueous solution as well as VOC from the gas phase. Two experimental conditions were suggested by the authors but in order to have a high mass yield and to reduce the energetic cost of the process, the optimal condition having 1.5 g of $\text{H}_2\text{SO}_4 \text{ g}^{-1}$ of sludge; 700°C and 145 min was suggested to be more appropriate. Besides these, various other materials such as human hair, pine needles, cactus leaves, polymer materials, ZnS , MnO_2 , black tea leaves, tree fern, pyrite and synthetic iron sulphide, alum impregnated activated alumina, calcined-alunite, sporopollenin-a biopolymeric material, coconut copra meal, husk of *Lathyrus sativus*, zeolitized pumice waste, regenerated clay mineral from spent bleaching earth, bauxite-a neutralized bauxite refinery residue, rosacina seeds, limestone and GAC mixture, and wheat bran

have also been explored as adsorbents. Other adsorbents such as a wood charcoal, red mud, sun flower stalks, petioles felt-sheath and rice husk have also been used for the adsorption of cadmium [142]. Certain waste materials from industrial or agricultural operations may be potential alternative biosorbents. In the last few years, adsorption has been shown to be an economically feasible alternative method for removing trace metals from wastewater and water supplies [143].

3. Bio-waste Mediated Synthesis of Nanoparticles

Plant-mediated biological synthesis of nanoparticles has acquired prominence only in the recent years [144]. Phumyinget *al.*, [145] reported the synthesis Fe_3O_4 nanoparticles using Aloe vera plant extract and high purity of formed nanoparticles was confirmed with XRD. The intermediate particle size calculated from XRD increased with an increase in temperature and time. Based on the correclivity, it was deduced that the nanoparticles were superparamagnetic in nature. Pandian and coworkers [146] formed Ni nanoparticles by using aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as precursor and leaf extract of *Ocimum sanctum* as reducing agent as well as stabilizing agent.

The Ni(II) ions were lessened into Ni(0) by hydrated electrons of *O. sanctum* aqueous leaf extract and Ni(0) nuclei were formed. These Ni(0) atoms then aggregate and Ni NPs were formed. A UV/Vis spectrum of the sample was registered and peak centered at 395 nm corresponding to Ni NPs confirmed the formation of Ni NPs. The XRD pattern was registered for Ni NPs confirming that Ni NPs have confronted centered cubic structure and intermediate particle size was 30 nm as calculated by Debye-Scherrer equation. Jayandran et al., [147] synthesized MnO nanoparticles by reducing manganese acetate with the help of easily available natural product, lemon extract as reducing agent and turmeric curcumin as a stabilizing agent. The curcumin was isolated from turmeric by using solvent extraction method and used for manganese nanoparticle stabilization. When an aqueous solution of $[\text{Pd}(\text{OAc})_2]$ was stirred with a methanolic extract of *Catharanthus roseus* for 1 h at 60°C, a change in colour occurred. It showed absorption peak in 360–400 nm range in UV-visible spectrum which corresponds to spherical palladium nanoparticles of ~40 nm. *C. roseus* extract is a mixture of eight compounds containing –OH groups which a lower the metal ion to metal nanoparticles. Synthesis, characterization and application of palladium nanoparticles as photocatalytic agent have been reported [148].

Palladium nanoparticles formed from aqueous leaf extract of *Hippophaerhamnoides* have been reported [149]. Thirumurugan et al. [150] have reported the biosynthesis of platinum nanoparticles from *Azadirachta indica* extract. TEM studies indicated the formation of polydispersed nanoparticles of small to large spheres (5–50 nm). The rate of platinum nanoparticle fabrication was increased with the increase in the

reaction temperature. FTIR spectrum showed sharp peaks at 1728.22, 1365.60 and 1219.01 cm^{-1} corresponding to the presence of carbonyls, alkanes and aliphatic amines, respectively. *A. indica* leaf broth was believed to contain the terpenoids which act as the reducing agent as well as stabilizer for the nanoparticles. Eggshells contain calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%). The high calcium content present assists in the formation of hydroxyapatite NPs. Banana is a favorite food worldwide and according to statistics which are not complete, more than 100 million tons of bananas is consumed worldwide every year and the husk is dumped as garbage.

This is composed of biopolymers such as cellulose, hemicelluloses, pectin, lignin and proteins and could be efficiently used for the synthesis of NPs. Hydroxyapatite NPs have been synthesized using banana husk. Pectin present in the husk plays a major role in the surface modulation of the NPs. Banana husk extract has also been used successfully to synthesize Mn_3O_4 NPs having super capacitive properties. Mn_3O_4 is one of most stable oxides of manganese which possesses broad range of interesting properties ranging from catalysis to high density magnetic storage medium [151]. SEM image depicts the agglomerated particles with an intermediate diameter of 20–50 nm. Zinc oxide nanoparticles were prepared using coriandrum sativum leaf extract and zinc acetate dihydrate. It was utilized as a photocatalyst for the degradation of anthracene. Optimum photocatalytic degradation of 100 $\mu\text{g L}^{-1}$ anthracene is 1000 $\mu\text{g L}^{-1}$ ZnO NP's, at ambient temperature (25°C), pH 7 and ultraviolet irradiation for 240 min. Under these conditions the percentage decomposition of anthracene is 96%. The kinetic study of the reaction obeys Langmuir–Hinshelwood model and fitted the pseudo first order rate constants. Formation of anthraquinone as a main decomposition product was confirmed by HPLC and gas–mass–spectrometry. This photocatalytic degradation reaction significantly reduces the toxicity of anthracene [152].

4. Conclusion

Applications of Bio-waste “agricultural waste” biosorbents for the removal of diverse type of pollutants from water have been reviewed based on a substantial number of relevant research articles published up till now. The use of “bio-waste” based biosorbents for removing various pollutants from water and wastewater offers many attractive features such as the outstanding adsorption capacity for many pollutants and the fact that these materials are low-cost, non-toxic and biocompatible. It is suggested that these may be used in future at large scale water purification. The green method of synthesis of nanoparticles is easy, efficient, and eco-friendly in comparison to chemical-mediated synthesis. The biological synthesis of nanoparticles using plant extracts plays an important role in the field of nanotechnology. The extracts of plants and spices may be capable of producing nanomaterials. This eco-friendly method could be a competitive alternative to the conventional physical/chemical methods used for

synthesis of nanoparticles and thus has a potential to use in water applications. Nanotechnology for water and wastewater treatment is gaining momentum globally. The unique properties of nanomaterials and their convergence with current treatment technologies present great opportunities to revolutionize water and wastewater treatment. There is a great concern to search for environmentally benign methods which results in the development of bio-nanotechnology. Green chemistry is beneficial due to eco-friendliness, economic prospects, feasibility, enhanced biocompatibility, low cytotoxicity, and high antioxidant and high antimicrobial activity of formed nanoparticles. These features help in the fields of environmental cleaning.

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