Valorisation of post-sorption materials: Opportunities, strategies, and challenges

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A R T I C L E   I N F O
Available online 12 December 2016

Keywords:
Post-adsorption
Post-sorbent
Exhausted sorbent
Spent sorbent
Adsorption
Biosorption
Fertilizers
Feed-additives
Catalysis
Carbothermal synthesis
Nanoparticles
Water treatment
Aqueous medium

A B S T R A C T

Adsorption is a facile, economic, eco-friendly and low-energy requiring technology that aims to separate diverse compounds (ions and molecules) from one phase to another using a wide variety of adsorbent materials. To date, this technology has been used most often for removal/recovery of pollutants from aqueous solutions; however, emerging post-sorption technologies are now enabling the manufacture of value-added key adsorption products that can subsequently be used for (i) fertilizers, (ii) catalysis, (iii) carbonaceous metal nanoparticle synthesis, (iv) feed additives, and (v) biologically active compounds. These new strategies ensure the sustainable valorisation of post-sorption materials as an economically viable alternative to the engineering of other green chemical products because of the ecological affability, biocompatibility, and widespread accessibility of post-sorption materials. Fertilizers and feed additives manufactured using sorption technology contain elements such as N, P, Cu, Mn, and Zn, which improve soil fertility and provide essential nutrients to animals and humans. This green and effective approach to managing post-sorption materials is an important step in reaching the global goals of sustainability and healthy human nutrition. Post-sorbents have also been utilized for the harvesting of metal nanoparticles via modern catalytic pyrolysis techniques. The resulting materials exhibited a high surface area (>1000 m²/g) and are further used as catalysts and adsorbents. Together with the above possibilities, energy production from post-sorbents is under exploration. Many of the vital 3E (energy, environment, and economy) problems can be addressed using post-sorption materials. In this review, we summarize a new generation of applications of post-sorbents as value-added green chemical products. At the end of each section, scientific challenges, further opportunities, and issues related to toxicity are discussed. We believe this critical evaluation not only delivers essential contextual information to researchers in the field but also stimulates new ideas and applications to further advance post-sorbent applications.

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1. Introduction

Development of sustainable materials and technologies is currently a popular research area in many fields of science. The three major factors that drive this area of research are: (i) environment, (ii) economy, and (iii) depletion of natural reserves. Due to the rapid population growth worldwide, there is a high demand for various commercial goods and products. A large number of these products contain metals (Fe, Cd, Cu, Pb, etc.) and materials (nano, plastic, etc.) that contribute to significant environmental pollution problems when they are discarded or damaged [1]. One notable example is the vast quantities of “e-waste” generated globally through discarded electric and electronic equipment, which will build up even more rapidly in the near future [2]. This waste contains various toxic metal ions, such as Al, Fe, Pb, Cd, Co, Cu, La, Ni, and Hg, along with traces of rare earth and elemental elements, such as Au, Ag, Sn, Se, Te, Pt, Pd, Ta, Co, and In [2–6], which, when released into the environment, cause severe health problems and environmental issues either directly or indirectly. Additionally, nanomaterials/nanoparticles used in various commercial products have become a serious concern [7]. Nanomaterials are one of the key ingredients in products such as sunscreens, cosmetics, photovoltaics, liquid magnets, automotive coatings, and more [8–10]. There is an ongoing debate about the safety and toxicity of nanomaterials because their fate and behavior in air, water, and soil environments have not been fully examined [11–20]. Iron (Fe) is one of the technologically important key elements that has different valence states (0, II, III, IV, V, and VI) and its polymorphs, such as Fe₃O₄ and FeO(OH), have been widely used around the globe for various industrial applications [21]. For instance, iron is commonly used in steel production by combining with other alloying elements [21,22]. Magnetic iron-based materials are of particular and emerging interest because of their facile separation property; and these materials have been used in various fields such as water treatment [23,24], food analysis [25], photocatalysis [26], electrochemical biosensing [27], magnetic hyperthermia [28], drug delivery [29], and sensors [30]. Nonetheless, there is still continuing discussion about the safety and toxicity of iron oxide nanoparticles [31–33]. High-tech materials are also of economic concern because manufacturing of most of these products requires very costly raw materials. Furthermore, the cost of these materials is increasing annually due to high demand; thus, it is important to find sustainable ways to reuse or recover these materials from products after their use. Additionally, because most of these materials are manufactured using naturally occurring resources, the limited reserves of these resources are rapidly being depleted [34]. For example, natural reserves of metal ions widely used in technology manufacturing have measurably decreased [35]. Although there are still untapped reserves, such as sea water, that could be a source of various critical metal ions [36], environmental, technical, and economic issues limit the practicality of mining from these sources [37–40]. The need for sustainable technologies and materials is more essential than ever in order to overcome these environmental, economic, and resource availability issues.

Adsorption is one of the most successful techniques in the field of separation science. Diverse solid materials (adsorbents) have been used to remove or recover a wide range of contaminants, including metal ions, dyes, organics, and pharmaceuticals (adsorbates) (Fig. 1). Charcoal and activated carbon are the most popular and widely used adsorbents for removing various contaminants, and these remain at the forefront for commercial applications. These materials can be disposed of easily, or sent to a landfill after they are no longer useful. However, although carbon-based materials show a high efficiency of binding organic pollutants, they have a limited tendency to bind inorganics. To overcome this limitation and to improve their performance, researchers have focused on the development of new and diverse adsorbent materials, such as zeolites, biosorbents, polymers, metal oxides, nanomaterials, chemically modified adsorbents, and others [41–48]. Most of the research into these adsorbent materials has focused on improved performance and increased removal rates, whereas less emphasis has been placed on the storage, disposal, and reuse of these adsorbents once they are spent. Some of the newer-generation adsorbent materials used in water treatment have been examined for possible toxic effects on living organisms [17,49–51]. Also of concern is the high cost of manufacturing particular adsorbents due to the need for expensive raw materials. Thus, in recent years, researchers have focused on the use of post-sorbents, which are sorbents with bound materials, for various applications to meet environmental, energy, agriculture, and dietary needs [52–55].

1.1. Adsorption

Adsorption is a naturally occurring phase transfer process and is widely used for the removal of adsorbates (molecules or ions) from fluid phase (gases or liquids) using adsorbent materials (typically solid). Using adsorption to remove notoriously toxic pollutants from the liquid (aqueous) phase has been one of the most widely employed techniques used to obtain clean water for drinking and for industrial purposes. Although the term “adsorption” was not coined until 1881, the process itself has been used for many years. Egyptians and Sumerians used charcoal for the reduction of copper, zinc, and tin ores in the manufacturing of bronze around the year 3750 BC [56,57]. In the year 1881, the term adsorption was introduced into the literature by H. Kayser, at the suggestion of E. du Bois-Reymond [58,59]. Prior to this, both absorption and the adsorption phenomenon were referred to as “absorption” [60]. The tremendous interest in adsorption has led to numerous publications including research reports, reviews,
monographs on historical evolution, and information about mechanisms and applications of adsorption many of which are referred herein [56,61–66]. Although adsorption can be used for a variety of applications, it has historically been used primarily for wastewater treatment to address both strict environmental regulations and the growing level of contaminants (heavy metals, dyes, pharmaceuticals, micro pollutants, biologicals and plastics) in water. Progress in designing and developing novel adsorbents with multi-functional properties has made adsorption a key technology in wastewater treatment (Fig. 2). The goals for development of these materials have focused on achieving a high sorption capacity, a rapid sorption rate, and high affinity. Therefore, the new generation of adsorbents now includes nanomaterials, composites, metal-organic frameworks, and layered-double hydroxides.

Review articles published in the past years have described the removal of organics, metal ions and dyes, and the overall number of reviews on adsorption is indicative of the importance of this field [67–87]. Individual reviews discuss the performance of particular adsorbent materials such as aerogels [76], biochar [68], biochar-based nano-composites [88], carbon nanotubes [71], chitosan [69], coal-based adsorbents [89], composite fibers [77], engineered nanomaterials [90], hydrogel [91], layered double hydroxides [67], magnetic chitosan composites [92], metal-organic frameworks [75,85,86], nanoadsorbents [70], nanocomposites [78,79,83], palygorskite [74], polymer-functionalized nanocomposites [83], polypyrrole-based adsorbents [73], and spinnel ferrites [81]. These reviews primarily describe the efficiency and performance of adsorbent materials in water treatment, and none of these discuss post-sorbent applications. Biomaterials (plant, microbial and agricultural wastes), which when used for adsorption are known as biosorbents, are also widely used to address contaminants problems because they are abundant in nature, low-cost and easily available. The process of biosorption is a very popular technique and involves the use of solid biomass for the removal/recovery of various toxic pollutants through various physico-chemical mechanisms. Although there are slight differences between adsorption and biosorption, we will use the term adsorption to refer to both processes throughout this review because the intention is to focus on post-sorbent applications of each.

1.2. Post-sorbents

Two separate terms are used to describe sorbents after they have been used: post sorbents and spent (exhausted) sorbents. Post-sorbent is a term used to describe a solid adsorbent concentrated with adsorbate ions or molecules that have been removed from dilute aqueous phase through the adsorption process. Spent or exhausted sorbent is the solid waste generated after adsorbate has been regenerated or recovered from adsorbent. The major drawback of adsorption is that this is a nondestructive technology; the adsorbate does not degrade or disappear when it is transferred from aqueous to solid phase. Thus, post-sorbent (adsorbate-laden sorbent) management is of utmost importance for the sustainability of adsorption technology. Current options for managing post-sorbents are limited to: (i) recovery of the sorbate, (ii) disposal in a landfill, and (iii) safe storage or disposal. Landfill disposal of post-sorbent (laden with toxic contaminants) leads to secondary pollution problems, such as soil, underground water, or surface water contamination through natural leaching or desorption [54]. Recovery of the sorbate (contaminant) from the sorbent is possible; however, this process has several disadvantages. Regeneration of adsorbents is dependent on factors such as the type of adsorbent, the adsorbate itself, adsorbate-adsorbent interactions, the treatment process, and the cost of the regeneration process. Most of the techniques used for sorbent regeneration, including the use of thermal energy [93], microwave irradiation [94], ultra-sonication [95], dielectric barrier discharge plasma [96], and others, have notable limitations. For example, spent activated carbon can be regenerated through thermal treatment, which reduces the active surface area and decreases the adsorption efficiency in subsequent adsorption cycles. When a harsh chemical compound, such as an acid or alkali, is used in the regeneration process, there are both economic and environmental consequences. For example, regeneration of a fixed-bed granular activated carbon comprises 75% of the total operation and maintenance cost [97]. Although adsorbents are recycled, inadequate or incomplete removal of the toxic adsorbate can occur. Additionally, stable adsorbent-adsorbate interactions limit the effectiveness of the recovery process when conventional solvents (acids, bases, and organic solvents) are used [98].

The two methods used to manage both post-sorbents and spent (exhausted) sorbent wastes are landfill disposal and incineration [99]. The factors that influence these methods include: (i) cost of the adsorbent, (ii) pollutant type, (iii) operating cost, (iv) cost of the combustion and incineration plant, and (v) fees for disposal. Although landfills have typically been used for the disposal of sorbents, this method has a subsequent pollution risk when toxic compounds leach from adsorbents into the soil. With this in mind, strict environmental regulations have been put in place. Both Spanish and U.S. EPA waste disposal guidelines prevent the disposal of metal- laden ashes in landfills [100]. Some of the newly developed adsorbents, such as nanoparticles, metal oxides, and composites, are themselves composed of toxic materials and metal ions. These have often been used as high-efficiency adsorbents for treating a variety of contaminants because of their high sorption capacities and rapid rates of adsorbent removal. The safety of these materials is a topic of debate because most cause problems when they enter air, soil, or water environments. Researchers have paid more attention to technology development and less attention to safe treatment and effective management of post-sorbents and spent adsorbents.

Adsorbent cost is another important issue because most of the emerging adsorbents are in the form of composites and hybrid materials that comprise two or more distinct cost-effective materials. For example, nanomaterials such as graphene/graphene, single-walled carbon nanotubes (SWCNTs), and multi-walled carbon nanotubes (MWCNTs), have been used to fabricate composite adsorbents [101–104], and the cost of these materials is in the range of $0.10 to $1000 per gram depending on the quality, grade, and functionalization [90,105]. The cost

Table 1

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Cost ($/kg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mag-PCMA</td>
<td>70 ± 4</td>
<td>[90,106]</td>
</tr>
<tr>
<td>Biochar</td>
<td>0.08−13.14</td>
<td>[107]</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>1−22</td>
<td>[108−110]</td>
</tr>
<tr>
<td>Granular activated carbon</td>
<td>3.30−6.71</td>
<td>[111,112]</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>6000</td>
<td>[111]</td>
</tr>
<tr>
<td>Graphene</td>
<td>990</td>
<td>[111]</td>
</tr>
<tr>
<td>Modified Ficus carica fibers</td>
<td>0.2</td>
<td>[113]</td>
</tr>
<tr>
<td>Polyampholyte hydrogel</td>
<td>6.3 × 10⁴</td>
<td>[114]</td>
</tr>
<tr>
<td>PSA−GO</td>
<td>6.93 × 10⁴</td>
<td>[115]</td>
</tr>
<tr>
<td>Amino siloxane oligomer−linked graphene oxide</td>
<td>8.08 × 10⁴</td>
<td>[115,116]</td>
</tr>
</tbody>
</table>

* Laboratory scale.
* Factory scale.
of some of the most commonly used adsorbents are listed in Table 1 and are estimated primarily from the cost of raw materials alone. A true estimation of the overall cost of an adsorbent includes the cost of raw materials, energy, labor, and processing. Additionally, safe management (storage or disposal) costs should be taken into consideration as well.

Adeleye et al. [81] thoroughly describe the costs and environmental issues regarding engineered nanomaterials used in water treatment processes. Adsorbent cost is one of the key factors that influences real-world industrial applications. As most of the emerging adsorbents are expensive to produce and some are potentially toxic themselves, reutilization is essential for useful application of these materials.

1.3. Objective of this review

A considerable amount of progress has been made in adsorption research with the aim of removing toxic pollutants from wastewater using a wide variety of adsorbent materials [80,102,117–119]. For an adsorption method to be sustainable, regeneration of the post-sorbent is a particularly important step. However, most of the existing technologies require the use of harsh chemicals, energy, and processing steps, and may limit the lifetime of the adsorbent itself. Thus it is essential to identify alternative ways to utilize post-sorbent materials as a value-added product. Numerous reviews have been published describing adsorption [68,81,92,120–124], but most of these focus on the performance of materials, sorption isotherm and kinetics, and mechanisms. Safety management and reuse or disposal problems associated with post-sorbents or spent adsorbents are rarely addressed. In fact, to date, few studies address the management of spent regenerated solutions, spent adsorbents and exhausted sorbent applications [54,125,126]. Reddy et al. [81] discusses the disposal problems associated with spent spinel ferrite adsorbents and their management. Gómez-Pastora et al. [125] review the management of spent magnetic adsorbents through regeneration and reuse. Dodson et al. [127] discuss the value-added applications of metal-loaded sorbents. It is necessary to find sustainable pathways for effective utilization of pollutant-loaded adsorbents as value-added products to resolve the economic, toxicity and management issues associated with these materials. In this review, we propose alternative strategies for the effective utilization of post-sorbents based on their emerging applications.

2. Post-sorbent applications

2.1. Fertilizers and soil conditioners

World food resources depend primarily on agriculture, and it is predicted that global agricultural production must increase by 70% by the year 2050 [128] to meet the demands of a rapidly growing world population (9.7 billion by the year 2050) [129–132]. To confront this global food demand, modern farming techniques that maximize agricultural production have been employed; however, these lead to depletion of carbon and nutrients in the soil. Crops cultivated in these overused soils become less productive [133] and cannot provide the essential elements required for a healthy human diet, and therefore lead to cases of micro- and macro malnutrition [131,134,135]. Dimpka et al. [136] comprehensively discusses the importance of micronutrients in effective agronomic production. Billions of people around the globe suffer from an insufficient intake of micronutrients due to mineral-deficient food crops [137]. Micro- and macro- malnutrition lead to diverse health effects, including mental retardation a weakened immune system, and an overall decrease in health [138]. A conference held in 2014 by the FAO/WHO (Rome, Italy) emphasized that deficiencies in essential dietary micronutrients affect more than two billion individuals around the world, with women and children particularly at risk [139,140]. At the conference, a Rome Declaration on Nutrition was formulated, with one goal being “the elimination of malnutrition in all its forms”. A reliable and appropriately balanced supply of micro and macronutrients is essential for enhancing plant growth and overcoming malnutrition problems [141].

Fertilizers have been widely used to enhance crop yields. Fertilizers are typically comprised of six macronutrients, including calcium (Ca), magnesium (Mg), phosphorus (P), nitrogen (N), potassium (K), and sulfur (S), along with eight micronutrients, including boron (B), chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), and zinc (Zn) [142]. The nutrients (micro or macro) are applied
in either organic or inorganic form to soils that are deficient. The use of fertilizer in agriculture is likely to increase considerably in the future [143]. The IFA (International Fertilizer Association) website reports that the global use of nutrient fertilizer (nitrogen, phosphate, and potash) is estimated at 186 million tons, and will reach around 200 million tons by the year 2018 [144].

Several studies demonstrate that excessive usage of fertilizers leads to the release of high concentrations of compounds such as nitrogen and phosphorus into the environment [143,145–147]. The enrichment of these nutrients in particular ecosystems can cause eutrophication, or lead to the excessive richness of nutrients in the water, likely due to run-off. This is detrimental to the environment as it results in a lack of oxygen that promotes plant growth while increasing animal mortality [34, 146,148]. The raw resources required for the production of N and P fertilizers are non-renewable. Furthermore, the limited natural reserves of these materials are being exhausted due to their widespread use as fertilizers [149–151]. Thus, effectively managed fertilizers application is essential.

A limited supply of nutrients leads to low crop production, soil degradation, and poor human nutrition; in contrast, high concentrations lead to environmental pollution [147]. The nutrient use efficiency (NUE) of crops is poor under realistic conditions. According to the IFA, in the first year of nutrient fertilizer application, the utilization rate for both N and K is about 50–60%, while only 10–25% for P [152]. The remaining unused nutrients are destined to degrade, release or leach, all of which may cause surface and groundwater pollution. The major disadvantages of using conventional fertilizers are low efficiency and excessive waste, thereby resulting in numerous severe environmental and health complications. Thus, for the sustainable management of fertilizers, it is critical to develop slow and controlled-release technologies (Fig. 5). The European Standardization Committee (CEN) Task Force stipulated that slow-release fertilizers should meet the following conditions at a temperature of 25 °C: (i) no > 15% release in 24 h, (ii) no > 75% release in 28 days, and (iii) at least 75% released by the stated release time [153].

Various techniques have been explored for use in regulating the quantity of nutrients that are discharged into water. Of these, sorption is one of the more proficient and economical practices and has the following benefits: ease of handling, a wide choice of adsorbents, minimal operation costs, less sludge release, and fewer disposal complications. Adsorption is the only technology for which it is feasible to use nutrient-laden adsorbents as fertilizer and soil conditioner in agricultural systems [154]. Compared to conventional fertilizers, sorption-based fertilizers offer several advantages: (i) soil-deliverability, (ii) controlled nutrient release, (iii) fewer adverse effects, (iv) biocompatibility, and (v) excellent nutrient use efficiency. The manufacturing of fertilizers using sorption technology would be more sustainable and economical because precursor materials used for nutrient loading are renewable (biomass, zeolites, biochar, and manure) and are available at low or no cost. However, the successful application of adsorbent as fertilizer relies heavily upon the choice of adsorbent materials because these will define the relevant properties, such as nutrient loading capacity, cost, nutrient release rate, adaptability to soil conditions, and water retention/holding capacity. Several specific adsorbents could be fabricated to load both cationic (NH₄⁺, K⁺), anionic (NO₃⁻, PO₄³⁻), and trace mineral (Cu, Fe, Mn, and Zn) nutrients in aqueous solutions, which could then be successfully applied as fertilizer (Fig. 6).

One of the most successful adsorbents used for fertilizer applications is biochar, a solid carbonaceous porous product acquired by partial combustion of organic materials using modern pyrolysis techniques [55, 155–157]. The biochar pore structure directly contributes to the soil porosity providing water, nutrient, and mineral storage and accessibility. Biochar exhibits typical pore structure which might be divided into three kinds such as macro, meso, and micropores as shown in Fig. 7. This division is based on pore sizes, large pore sizes >50 nm are macropores, pore size in the range of 5–20 nm are mesopores, whereas smaller pore size in the range of <2 nm are micropores. The micropores in biochars have high sorption ability for small molecules [158], thus during soil applications biochars with high micropores might reduce the nutrient loss during volatilization of organic molecules.

Biochar has been widely used to improve soil fertility and soil carbon sequestration in soil amendment fields, which generally improves soil quality and helps to mitigate processes associated with climate change [159–161]. Utilization of biochar has received global attention in the past few decades and several reviews on this application have been published [162–168]. The soil organic carbon (SOC) levels that are essential for plant growth have decreased around the world due to intensive agricultural activities. Biochar, derived from carbon-rich biomass, has a high organic C content that could enhance SOC levels. According to published reports, the carbon content of biochar can reach 70%, depending on the feedstock material [169]. Soil containing biochar has been shown to have measurable improvements in water-holding capacity, structure, and porosity, cation exchange capacity, electrical conductivity, and leaching of nutrient and agrochemicals [170–174]. Not only can biochar improve the growth of plants through its natural mineral/nutrients composition, it also protects plants from the abiotic stress of toxic elements and organic pollutants by adsorbing or precipitating toxic pollutants [175]. Biochar can be manufactured from a wide-range of materials that are of low to no cost because they are typically discarded as waste. These include: agricultural wastes, animal manure, forest waste, and sewage sludge. For all of these reasons, several researchers have focused on the application of biochar as a sorbent for the recovery/enrichment of nutrients and its subsequent application as fertilizer. Although biochar is one of the strategic key resources that have been used to enhance soil fertility, it does not show the same performance and effectiveness under all conditions. This inconsistency is because the physicochemical characteristics of biochar depend upon the properties of the feedstock materials (available nutrients, carbon content, and porosity) and the pyrolysis conditions (time and temperature) that are used. The nutrient (both micro and macro) availability of biochar-amended soil depends on several physical and chemical properties, such as pH, surface area, porosity, cation exchange capacity (CEC), and the transfer of nutrients into the amended soil. However, it is possible to prepare custom or engineered biochars in such a way that they function effectively under specified conditions.

A major drawback of biochar is that it is ineffective at recovering nutrients, because most nutrients (nitrate and phosphate) are anionic, while the surface of biochar is highly negatively charged. In one study, thirteen different biochars derived from various feedstocks were tested for nitrate or phosphate adsorption, and most exhibited little or no sorption ability [176]. Similar results were observed with nine other biochars prepared from different feedstock materials [177]. These two
studies demonstrated that the nutrient sorption ability of biochar significantly differs with biochar type and nutrient kind. To improve the anionic nutrient sorption ability of biochar, composites were manufactured by combining inorganics, such as Al, Ca, Mg, Fe, La, Ca-Mg, and Mg-Al, with biochar [178–188]. Efforts were focused on the development of Ca and Mg biochar nanocomposites because these have attractive properties such as biocompatibility, high surface area, high nutrient loading capacity, and controlled release of nutrient. Mg-enriched tomato tissue has been used as an engineered biochar for phosphate recovery from aqueous solution and then repurposed as a soil P-fertilizer [55]. Results of post-sorption characterization revealed that both precipitation and surface deposition are key mechanisms involved in P recovery. Bioassay results showed that the addition of P-loaded biochar nanocomposite improved seed germination rates from 53% to 85% (p < 0.001). To enhance the anionic sorption capacity and improve the ease of separation of biochar from aqueous solutions, magnetic MgO-decorated biochar was manufactured using ferrous chloride, and magnesium chloride, and subsequently tested for phosphate recovery and reuse [156]. Mg content during impregnation increased from −0.44% to 20%, and, at an Mg content of 20%, the biochar had a high phosphate sorption capacity. The sorbate-sorbent interactions were attributed to protonation, surface electrostatic attraction, surface inner-sphere complexation, and precipitation.

Biochar characteristics may vary significantly with pyrolysis temperature, which further influences the sorption ability of biochar [189–191]. In one study, the effect of pyrolysis temperature (200–800 °C) on the characteristics and phosphate sorption ability of biochar prepared using Undaria pinnatifida roots as feed-stock were investigated [192]. The results revealed that when pyrolysis temperature increased, the following were observed: (i) decreased yield, (ii) increased aromaticity, and (iii) decreased polarity. Phosphate sorption increased with pyrolysis temperature up to 400 °C, and then decreased as the temperature was further increased. When the efficiency of phosphate-loaded biochar fertilizer was studied using potted indoor lettuces, the pot with supplied biochar grew faster, had a larger leaf area and size in the first 21 days, and had larger and wider leaves after 30 days as compared with control plants grown with commercial compost [192]. Biochar as a soil conditioner was also examined in a study using ammonium-laden corn cobs [193]. The biochars were manufactured at two different pyrolysis temperatures, 400 and 600 °C, and biochar prepared at the lower temperature had a higher sorption capacity than that prepared at the higher temperature.

Zeolite and clays, which are abundant in nature, have also been used extensively for nutrient recovery and subsequently as fertilizers [194–197]. Citing the advantages of air permeability, good soil osmosis, and water storage efficiency, a recent study reported the use of Kanuma and Akadam clays, along with zeolites, to manufacture ceramic adsorbent for the recovery of ammonium that was then repurposed as a fertilizer [198]. A maximum nitrate sorption capacity of 75.5 mg/g was obtained using an initial concentration of 10,000 mg/L NH₄⁺-N.

As a demonstration of the value of the high nutrient loading ability of composite materials, a 30%, palygorskite nanocomposite, that was manufactured using carboxymethyl chitosan, acrylic acid, and palygorskite, exhibited a high ammonium loading capacity of 237.6 mg/g [199]. The composite exhibited both slow-release of nitrogen, with 60% of the nitrogen released into the soil over the course of ten days, and good water-retention properties. In addition to nitrogen, palygorskite composites also contain nutrients such as P, K, Ca, Fe, Mg, and Mn, which are useful for plant growth. In another study, six surfactants comprised of functionalized and unmodified synthetic silicate were manufactured and used for the recovery and reuse of anionic nitrate [200]. Surfactant-loaded clinoptilolite had a sorption capacity of 125 mg/g, which was higher than other unmodified and modified silicates. The results also showed that surfactant-modified silicates were effective as fertilizers due to their slow release performance, wherein nitrate continued to be released after 15–20 days of observation. The same group also employed surfactant-modified silicates for phosphate removal and for application as a slow release fertilizer [201]. Phosphate sorption was efficient at pH 7 and a maximum sorption capacity of 93.46 mg/g was measured for hexadecyltrimethylammonium bromide-modified clinoptilolite. The sorption mechanisms between phosphate and surfactant-modified silicates were identified as electrostatic attraction, van der Waals interactions, and interlayer adsorption. Nutrient leaching studies in soil-column tests showed phosphate leaching after 15 days, demonstrating the slow-release characteristics of surfactant-modified silicates.

In addition to the above materials, biomass such as wheat straw [202,203], chicken feathers [204], waste biomass [205], seaweed [206], and spent mushrooms [207,208], has been utilized for nutrient loading and then reused in fertilizer applications. In one study, straw cellulose adsorbent was prepared and used for the recovery of both cationic (NH₄⁺) and anionic (H₂PO₄⁻) nutrients from aqueous solutions [209]. Soil experiments were performed to evaluate the slow-release behavior and water retention capacity of nutrient–loaded sorbent, and the results were positive; 95.1% N was released within 20 days, 60.0% P was released within 30 days, and when fertilizer dosage was increased from 0.5 to 2 wt%, the soil water–retention capacity was improved. In another application, recognizing the importance of Mg in phosphate sequestration Wang et al. [210] prepared a hybrid artemia shell–Mg adsorbent by
impregnating magnesium nitrate into artemia shells in an in situ process. Phosphate sorption experiments revealed a maximum sorption capacity of 32.7 mg/g at pH 6.4–6.9. The post sorbent (shell-Mg-P) has a slow-release behavior; only 65.8% of the phosphate had been released after 30 days. In addition to nitrogen and phosphorous other micronutrients including Mn(II) and Zn(II), have also been recovered and repurposed as fertilizer. In one study, spent mushrooms were converted to fertilizer on a pilot plant scale by loading Zn(II) and Mn(II) elements using sorption-based technology [207]. The biomass exhibited a sorption capacity of 15.84 mg/g for Zn(II) and 11.81 mg/g for Mn(II). Another study incorporated feather protein, extracted from chicken feathers, as the basic macromolecular skeletal material for manufacturing hydrogel sorbent and used this sorbent for the removal of cationic ammonium and anionic phosphate [204]. The authors propose that the resulting nutrient-laden sorbent could be utilized further as fertilizer. A summary of the adsorbents that have been used as fertilizers, the target nutrients recovered, and their applications are presented in Table 2.

Very little research has addressed the utilization of sorbent loaded with macronutrients (nitrogen, phosphorous) as fertilizers and soil conditioners, and few studies have evaluated the efficiency of micronutrient-loaded sorbents as fertilizers. However, recent attention has turned towards health-related issues associated with malnutrition attributed to micronutrient deficiency [219–221]. For instance, a zinc deficiency in the diet of people in developing countries is one of the 10 key issues contributing to health concerns according to the World Health Organization (WHO) [222,223]. This micronutrient deficiency can be overcome through supplementation of soils with fertilizers. For example, in the 1970s in Finland, it was determined that people were consuming an extremely low amount of Se (0.025 mg/day), and this led to a recommendation, put forth in 1984, to utilize sodium selenite multi nutrient fertilizers [224]. Since 1985, most fertilizers in Finland have included Se, and currently, all crop fertilizers contain 15 mg Se/Kg. Thus, it is conceivable to pinpoint a nutrient deficiency in a particular geographic location and address the problem by developing customized, nutrient-loaded sorbent fertilizers that provide the optimal supplementation. In another example, anemia, which is a significant global health problem affecting 1.62 billion individuals worldwide [225], is frequently caused by an iron deficiency [226,227]. Anand et al. [228] reported that iron deficiency anemia is one of the chief public health complications in developing countries such as India. Insufficiencies of minerals, specifically iron (Fe), zinc (Zn), and calcium (Ca), are a major problem in developing countries where they lead to adverse effects on human health [229]. Again, the possibility of manufacturing custom-tailored post-adsorbents (laden with essential trace elements) that can then be used as multi nutrient fertilizers may be a solution that leads to improve public health. Zeolites are ideal substrates for this purpose because they carry nutrients and release them gradually; they also have hydration and dehydration capacities that are helpful for maintaining water balance [197]. Zeolites possess selective adsorption efficiency for ammonia (NH₄⁺), which is useful in the manufacturing of nitrogen-based fertilizers [230]. The specific adsorbent-nutrient interactions and the nutrient release rate are both important properties to consider. Additionally, the following strategic points are important to consider when manufacturing nutrient-loaded sorbent fertilizers: (i) affinity for both cations and anions (NH₄⁺, K⁺, NO₃⁻, and PO₄³⁻), (ii) stability under soil environmental conditions, (iii) slow-release characteristics, (iv) water-holding capacity, and (v) ability to function for long periods of time. Although adding post-sorbent (nutrient-loaded sorbents) to soil improves agricultural yields and nutritional qualities (on a laboratory scale), socio-economic conditions will determine whether or not the

Table 2  
Sorption based fertilizers (nutrient-loaded adsorbents) and their characteristics.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Nutrient</th>
<th>Sorption capacity (mg/g)</th>
<th>Post-sorption applications</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engineered biochar</td>
<td>Phosphate</td>
<td>116.600 ± 26.590</td>
<td>Seed germination (85%)</td>
<td>55</td>
</tr>
<tr>
<td>MgO decorated biochar</td>
<td>Phosphate</td>
<td>121</td>
<td>Ryegrass seeding growth</td>
<td>156</td>
</tr>
<tr>
<td>Porous MgO-biochar nanocomposites</td>
<td>Phosphate</td>
<td>835</td>
<td>–</td>
<td>184</td>
</tr>
<tr>
<td>Mg/Al layered double hydroxide functionalized biochar</td>
<td>Phosphate</td>
<td>81.8</td>
<td>Proposed as fertilizer</td>
<td>186</td>
</tr>
<tr>
<td>Ca-Mg biochar</td>
<td>Phosphorous</td>
<td>327</td>
<td>–</td>
<td>187</td>
</tr>
<tr>
<td>Undaria pinnatifida roots</td>
<td>Phosphate</td>
<td>32.6</td>
<td>Lactuco sativa plant growth</td>
<td>192</td>
</tr>
<tr>
<td>Corn cob</td>
<td>Ammonia</td>
<td>6.37</td>
<td>Soil conditioner</td>
<td>193</td>
</tr>
<tr>
<td>Ceramic adsorbent</td>
<td>NH₃–N</td>
<td>75.5</td>
<td>Soil conditioner</td>
<td>198</td>
</tr>
<tr>
<td>Polygorskite nanocomposite</td>
<td>NH₄</td>
<td>238</td>
<td>Soil fertility</td>
<td>199</td>
</tr>
<tr>
<td>Surfactant modified silicates (HDTMAB loaded clinoptilolite)</td>
<td>Nitrate</td>
<td>125</td>
<td>Soil fertility</td>
<td>200</td>
</tr>
<tr>
<td>Surfactant modified silicates (HDTMAB loaded clinoptilolite)</td>
<td>Phosphate</td>
<td>93.5</td>
<td>Soil</td>
<td>201</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>Ammonium</td>
<td>7.15 mmol/g</td>
<td>Soil conditioner</td>
<td>202</td>
</tr>
<tr>
<td>Spent mushroom</td>
<td>Mn(II)</td>
<td>11.8</td>
<td>Proposed as fertilizer</td>
<td>203</td>
</tr>
<tr>
<td></td>
<td>Zn(II)</td>
<td>15.8</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Straw cellulose</td>
<td>NH₄Cl</td>
<td>68</td>
<td>Soil</td>
<td>209</td>
</tr>
<tr>
<td>Artemisia egg shell</td>
<td>H₂PO₄</td>
<td>38.6</td>
<td>Soil</td>
<td></td>
</tr>
<tr>
<td>Ca impregnated ramie biomass</td>
<td>Phosphate</td>
<td>32.7</td>
<td>Mung bean seedling growth</td>
<td>210</td>
</tr>
<tr>
<td>Fe-Mn binary oxide nanoparticles</td>
<td>P</td>
<td>259</td>
<td>–</td>
<td>211</td>
</tr>
<tr>
<td>CMC stabilized Fe-Ma nanoparticles</td>
<td>298</td>
<td>–</td>
<td>–</td>
<td>212</td>
</tr>
<tr>
<td>Starch stabilized Fe-Mn nanoparticles</td>
<td>313</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Surfactant-modified zeolite</td>
<td>Phosphorous</td>
<td>454.5 mmol/g</td>
<td>Soil conditioner, P nutrient</td>
<td>213</td>
</tr>
<tr>
<td>Natural zeolite</td>
<td>Ammonia</td>
<td>6.89 ± 0.64</td>
<td>Cultivation of A. platensis</td>
<td>214</td>
</tr>
<tr>
<td>Surfactant-modified zeolite</td>
<td>Nitrate</td>
<td>91 mmol/Kg</td>
<td>Sweet corn (Zea mays) plant growth</td>
<td>215</td>
</tr>
<tr>
<td>NiAl layered double hydroxide</td>
<td>Phosphate</td>
<td>49</td>
<td>Seaweed growth</td>
<td>216</td>
</tr>
<tr>
<td>Manure/waste 1:3</td>
<td>Zn(II)</td>
<td>225 mmol/Kg</td>
<td>Correct soil acidity and</td>
<td>217</td>
</tr>
<tr>
<td>Anaerobically digested sewage sludge and ochre</td>
<td>Phosphorus</td>
<td>6.70</td>
<td>Proposed as fertilizer</td>
<td>218</td>
</tr>
</tbody>
</table>
materials can be applied to commercial agriculture. The key issues that influence the application of post-sorbent fertilizers are the availability of feedstocks, the technology to manufacture fertilizer, and investment capacity. Further economic analyses of the use of post-sorbent fertilizers will determine the feasibility of applying these materials to agricultural systems. A recent cost analysis for manufacturing mushroom material loaded with Zn(II) and Mn(II) estimated $4.76/kg for the production of 100 kg/day in the pilot plant [207]. The cost of raw materials significantly influences the overall post-sorbent fertilizer manufacturing cost; thus, low-cost sources should be explored. Nutrients loaded onto adsorbents are expensive; however, these metal ions are plentiful in particular water sources at low or no cost. Seawater and wastewater, which are rich in various trace metal ions, should be considered as sources of micronutrients for sorption technology because this will decrease the costs of manufacturing nutrient-laden sorbents [36,231–233]. This strategy will be useful in two-ways: one, to remove toxic metal ions from wastewater, and two, to reuse these metals. In one study, poultry litter containing P was used as a source of nutrients, and Fe–Mn binary oxide nanoparticles were used to control the leaching of the P with an estimated treatment cost at $0.0036–0.0056/kg [212]. Composite materials as sorbents have also been developed using several types of metal oxide nanoparticles, such as MgO, which is widely used to fabricate biochar composites. For preparing MgO composite materials, alternative sources of Mg should be explored. In one study, carbon materials with stabilized MgO nanoparticles (~17–18 nm) were manufactured using an MgCl2 solution using the average Mg concentration in seawater, i.e. 1540 mg/L [234]. Utilization of untapped reserves to manufacture nutrient-loaded sorbent fertilizers will invariably reduce the overall product costs. A comprehensive assessment of the economic, technical, and environmental strengths and weaknesses of post-nutrient laden fertilizer manufacturing technologies should be carried out to determine the extent of the real-world applications for these materials.

It is important that post-nutrient laden sorbent fertilizers be examined for toxic characteristics that would limit their validity and application. For example, to enhance both nutrient loading capacity and controlled release properties, several researchers have employed nano-composite fertilizers. However, in recent years there has been much debate about the environmental safety and toxicity of nanoparticles [235–238]. Biochar has been manufactured as nano-composites using metal oxide nanoparticles such as CuO, CoFe2O3, MgO, MnO, and TiO2 to enhance the sorption performance, and the environmental and biological risk of these metal oxides needs to be considered [42,88]. It is essential to evaluate the stability and toxicity of newly manufactured nanocomposites. A measure of metal ions leaching from nanocomposites carried out using the U.S. EPA Toxicity Character Leaching Protocol (TCLP) will provide an indication of their behavior [239]. To pinpoint any adverse effects of nanocomposite fertilizers on health, it will be necessary to examine issues such as the fate and transport of the nutrient loaded nanocomposites in the soil, the ecosystem, the uptake and accumulation in plants, and the evolution of the toxicity of nanomaterials. Risk assessment studies should be conducted before any agricultural application is considered, and subsequent effects should be monitored continuously throughout the application.

Although biochar has a wide variety of benefits, such as improved soil fertility, improved plant growth, and increased crop yields, the possibility of negative consequences should also be considered. For example, the micronutrients mentioned above (essential elements) are required in trace quantities for normal plant growth, but when present at higher concentrations, these elements are toxic to living organisms. Before these nutrients are applied as fertilizers via post-adsorbents, the materials should be evaluated to assess whether or not toxic compounds, such as heavy metals, would be released into soils, thereby violating current environmental protocols. Biochars have been engineered from various organic feedstock materials, which may not only contain carbon, nutrients, and minerals, but also potential toxic elements (PTEs) such as Pb, Cd, Cu, and As. These materials also contain polycyclic aromatic hydrocarbons (PAHs) and highly volatile organic compounds (VOC), which are notable because of their adverse effects on plant growth and on microbial communities [240,241]. However, after converting feedstock into biochar, the PTE content was reported to be either low or high with respect to their feedstocks [242,243]. Although small quantities of bioavailable PTEs are expected in soils, the subsequent negative effects on crops are undesirable and leads to downstream effects on the health of animals and humans [244,245]. Furthermore, the practice of pyrolysis may alter the oxidation state of some PTEs, specifically Cr(III) or Cr(VI), which could significantly increase or decrease toxicity. Because the toxicity of biochar depends on pyrolysis temperature, Lyu et al. [191] investigated the toxic effects of biochars produced at temperatures ranging from 200 to 750 °C. They noted that biochars manufactured at pyrolysis temperatures ≥ 400 °C are less toxic and are more appropriate for soil usages. There are no legislative standards limiting PTE concentrations in biochar that is to be applied to soils. Instead, biochar containing materials are to be certified according to the International Biochar Initiative (IBI) guidelines [246], and the European Biochar Certificate guidelines [247]. These certificate systems were established by researchers as a preliminary assessment of the toxic characteristics of biochar materials. According to the IBI, the PTEs that are a concern in biochar include As, Cd, Cr, Co, Cu, Pb, Hg, Mo, Ni, and Zn, and Co and Mo [246] are also priority pollutants as per the U.S. EPA [248,249]. The European law on EC fertilizers suggests that heavy metals should not be purposely added to ammonium nitrate fertilizers, and the concentration of copper should be below 10 mg/kg [250]. Thus it is essential to investigate the concentrations of PTEs in biomass-based materials that are manufactured from new feedstock materials according to the extant legislation or regional regulations. These strategies will ensure the development of environmentally-friendly post-sorbent material enriched for nutrients, and will ensure that the application of these materials as fertilizers will improve the nutrient efficiency of crops and play a positive role in reaching the 2050 food and environmental security goals [146,251,252]. The industrialization of post-sorbent materials that are manufactured by sorbing nutrients onto various sorbents as fertilizers have been limited by the following key issues, (i) release of toxic metal ions from sorbent and/or composite sorbents causes antagonistic effects on plant growth, (ii) uncontrolled release of sorbed metal ions, (iii) cost, (iv) high volumes are required due to the lower amounts of sorbed nutrients compared with commercial fertilizers, and (v) uneven distribution of sorbed metal ions results either high or low nutrient availability.

2.2. Carbon-encapsulated metal nanoparticles (CEMNs)

Before providing a detailed account of the applications for post-sorbents in manufacturing carbon-encapsulated metal nanoparticles, it is relevant to introduce three major problems encountered in three divergent scientific fields (stable carbon-nanomaterial fabrication, biomass gasification, and wastewater treatment), all of which were solved through post-sorption technology. First, the preparation of stable metal nanoparticles is difficult. Pure metal nanoparticles (MNsPs), such as non-precious 3d-block transition metals (Fe, Cu, Co and Ni) and their alloys (CoFe, CoNiFe, etc.), have charmed researchers for years due to their optical, catalytic, magnetic, mechanical, photo-thermal, and electrical properties [253]. These interesting characteristics have led to stimulating applications in diverse areas such as nanosensing, nanocatalysis, water treatment, drug delivery, spectroscopy, magnetic resonance imaging, and plasmonics [253–257]. However, the high surface-to-volume ratio of pure metal nanoparticles is also associated with instability via oxidation in air, dissolution in acid, and aggregation due to high surface energy, leading to the deterioration of their magnetic properties among other things [258]. This restricts hands-on applications and creates difficulties in assessing the properties of these
materials [259–262]. Thus, inert materials, either organic or inorganic, have often been used to coat pure metal nanoparticles through in-situ and ex-situ techniques, in order to shield them from oxidation and to avoid changes in their properties. Encapsulation of highly dispersed metal/metal oxide nanoparticles within carbon materials is a useful method; the carbon layer protects the naked nanoparticles from oxidation, agglomeration, and harsh chemical environments, and maintains high magnetization [263]. Compared with other types of coatings, carbon provides the unique advantages of high chemical and thermal stability, high dielectric permittivity, magnetic permeability, better conductivity, and biocompatibility [264–268]. Carbon-encapsulated metal nanoparticles (CEMNPs) are a novel type of nanostructured carbon materials that have a unique core-shell construction consisting of metal cores surrounded by thin carbon coat (shells) (Fig. 8), and the crystallinity of this coating is graphic in nature and similar to CNTs [269,270].

CEMNPs have attracted much attention due to their unique physical and chemical properties, especially for application in catalysis, drug delivery, water treatment, and hyperthermia, as well as in information technologies such as magnetic data storage, xerography, electronics, and biomedicine [271,272]. There are several methods available for fabricating CEMNs; these include high-temperature annealing [271], chemical vapor deposition [273], arc discharging, and modified arc discharging [274]. However, in situ generation of nanoparticles using metal ion loaded biomass through carbothermal reduction is of particular interest due to the renewability of biomass, and also due to its economic and eco-friendly nature.

Preparation of stable carbon-nanocomposites for the treatment of contaminated water is another problem, which was also solved using post-sorption technology. The general manufacturing process for composites involves synthesis of carbon and nanoparticles individually, and then further mixing of these two distinct phases to obtain the composite materials. This approach has limitations, including: (i) the challenges of carbon manufacturing, which requires high temperature, high voltage, and is difficult to control, (ii) the poor stability and high cost of composites, and (iii) the undesirable impregnation of particles or adherence to surfaces and pores. Additionally, when composites are used in water treatment and come into contact with acidic solutions, there is a possibility of nanoparticle leaching. When composites are manufactured through the pyrolysis of biomass loaded with metal ions (post-sorbent), the nanoparticles that are harvested are held tightly inside the carbon (during the in situ generation of nanoparticles which are covered by the carbon). Thus, there is less chance of leaching, agglomerating or oxidizing. The process of post-sorbent pyrolysis is further advantageous because the manufactured composite is eco-friendly and the process is scalable and economically viable. The economic benefit of this approach is attributed to the use of low-cost biomass as the carbon precursor. The process is facile in that it occurs in just a few steps: (i) loading of metal ions (ii) drying (iii) pyrolysis, and (iv) washing. Depending on the process conditions, materials prepared in this way exhibit a high surface area of > 1000 mg/g [275].

The third problem that was solved using the post-sorbent pyrolysis technique was biomass gasification. Biomass is inexpensive and is an abundant renewable source of carbon that has recently been widely used as renewable source of energy and fuel production through a thermochemical conversion process. Production of synthesis gas (also termed as syngas) through gasification/pyrolysis is a promising technique to convert biomass into value-added chemicals, hydrogen, gas fuels, liquids, and char. Moreover, the generation of syngas compounds (H2, CO, CO2 and N2) through the gasification process also produces undesirable by-products, such as tar (comprising of benzene, naphthalene, phenol, toluene, and xylene) and inorganics (S, K, P etc.). Tar, comprised of benzene and polycyclic aromatic hydrocarbon, is of major concern because it is an environmental pollutant, and it damages process equipment, engines and turbines [276,277]. For effective use of syngas, these impurities, particularly tar, must be removed or treated. Catalytic reforming/cracking of the tars and hydrocarbons is an efficient technique that provides additional syngas, enhanced H2 content, high heating values, and higher biomass carbon utilization [278]. Transition metal-based catalysts, chiefly nickel-based catalysts, are effective in tar reduction and syngas reforming during biomass pyrolysis/gasification [279–281]. Among the different catalyst integration strategies, insertion of the catalyst metal precursor into the biomass (metal-impregnated biomass) through adsorption prior to thermo-chemical conversion was effective, and had a significant effect on the yields of tar, gas, and char [282–284]. Adsorption plays an important role in the preparation of metal-impregnated biomass because the chemical functional groups present in biomass act as adsorption sites during the impregnation step, and mineral cations present in biomass are also replaced by catalyst metal precursors through ion exchange [282,284]. High yield and good dispersion of the metal precursor are accomplished using this approach.

Biomass is an abundant carbon source that can be used as a precursor for manufacturing CEMNs. Biomass and derivative materials have been used widely in water treatment for the removal of metal ions from aqueous solutions, because they are abundantly available, low cost, and environmentally-friendly [120,285–290]. Biomass materials contain numerous oxygenated functional groups, such as carboxyl, carboxyl, amine, hydroxyl, and ether groups [291]. These functional groups act as ligands for metal ion complexation in aqueous media. Robalds et al. [292] classified the biosorption mechanism and their review and references therein are recommended for further reading on this subject. Due to the ability of biomass to form complexes with metals, it functions as a natural biotemplate to generate dispersed metal ions. In this respect, biomass has been used as both a template and a carbon source for harvesting nanoparticles. Recently, there have been several attempts to fabricate carbonaceous metal nanoparticles using the abundant, economical and environmentally friendly metal-loaded biomass (post-sorbent) as a precursor material.

This process involves the adsorption of transition metal ions (Cu, Ni, and Co, etc.) onto biomass, and then conversion to carbonaceous metal nanoparticles using catalytic pyrolysis/gasification techniques. Catalytic biomass gasification is an effective technique used to convert metal-loaded biomass into carbon, char, syngas, and nanoparticles. Harvesting carbonaceous metal nanoparticles involves the following processes: (i) sorption of metal ions onto biomass, (ii) grinding and drying, (iii) pyrolysis of metal-laden biomass, and (iv) in situ generation of metal nanoparticles. In the first step, the target metal cations are adsorbed onto the numerous oxygenated groups (hydroxyl, carboxyl, amine etc.) of

**Fig. 8.** Effect of air exposure and encapsulation of metal nanoparticles (MNP).
the biomass while in aqueous solution, and at the same time metal ions are dispersed inside the biomass matrix. In the second step, the biomass is thermally decomposed, and the major reactions that occur during thermo-chemical conversion are summarized in the following equations [293]:

\[
\begin{align*}
\text{C}_6\text{H}_4\text{O}_2 & \rightarrow (\text{H}_2 + \text{CO}_2 + \text{CO} + \text{CH}_4 + \text{C}_2 + \ldots) + \text{Tar} + \text{Char} + Q \\
\text{C}_6\text{H}_4\text{O}_2 + 2\text{H}_2\text{O} & \rightarrow \text{CO}_2 + (2x + \frac{y}{2})\text{H}_2 + Q \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2 - 41.2 \text{ kJ/mol} \\
\text{C} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + 3\text{H}_2 + 131.3 \text{ kJ/mol} \\
\text{C} + \text{CO}_2 & \rightarrow 2\text{CO} + 162.4 \text{ kJ/mol} \\
\text{CH}_4 + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + 3\text{H}_2 + 206.3 \text{ kJ/mol}
\end{align*}
\]

\(\text{C}_6\text{H}_4\text{O}_2\) represents the major types of biomass molecules, which include aldehydes, ketones, alcohols, carboxylic acid, and cresols. Adsorbed metal ions in the biomass matrix are reduced by the reducing components in the reaction (ex. \(\text{CO}, \text{CH}_4, \text{H}_2, \text{C}_6\text{H}_4\text{O}_2\) and bio-char). The carbothermal reduction of metal oxides is a well-known technique [294]. In the absence of oxygen, the abundant reductants molecules reduce the high-valency (\(\text{M}^{n+}\)) metal ions dispersed in the biomass into metal nanoparticles (\(\text{M}^0, \text{M}^{2+}, \text{MO, MFe}_2\text{O}_4\)). The carbothermal reduction of metal ions is described in the following equations:

\[
\begin{align*}
\text{M(NO}_3)_2 + 2\text{H}_2\text{O} & \rightarrow \text{M(OH)}_2 + 2\text{HNO}_3 \text{ or MO (7)} \\
\text{MO(s) + 3(H}_2\text{O, CO, C)} & \rightarrow \text{M(s) + (H}_2\text{O, CO}_2, \text{CO)}\text{†} \quad \text{(8)}
\end{align*}
\]

The advantages of this process are: (i) the metal nanoparticles and the carbon can be harvested simultaneously, (ii) the metal compounds have a catalytic effect, and (iii) it is a one step process. Catalytic biomass gasification was principally used to obtain synthesis gas, bio-oil, bio-char, and \(\text{H}_2\) [295]. For further reading on carbon-based nanoparticles, including carbothermal synthesis, catalytic biomass gasification, biomass pyrolysis, and carbon supported catalysts, see other reviews on the subject [157, 296–303]. A schematic of carbon-nanoparticle harvested through carbothermal-reduction is shown in Fig. 9.

**Fig. 9.** Synthesis of carbon-nanoparticles through carbothermal synthesis.

In situ generation of nanoparticles through biomass pyrolysis/gasification depends upon biomass composition, metal ion impregnation, and pyrolysis conditions. Few of the significant factors, such as effects of metal ions, metal salts, and impregnation conditions (pH, atmosphere, and vacuum), have been reported [278, 282, 304–306]. pH is one of the key parameters that influences metal speciation in aqueous solutions, and it influences the functional groups that are present on the biomass [307, 308]. Biomass consists of surface chemical groups such as carboxyl, carbonyl, hydroxyl, amine, amide, phosphate, etc. [291], and these groups act as sorption sites. The pH influences the charges of these sorption sites. As the pH decreases, the biomass functional groups are protonated due to the high concentration of protons. This situation is not favorable for the sorption of positively charged metal ions due to the electrostatic repulsion. In the other hands, as the pH increases, the number of negatively charged sites increases, facilitating sorption of cations. Furthermore, the pH also influences the complexation process which involves the formation of coordination bonds between metal ions and functional groups containing a lone pair of electrons [287]. This complexation process is highly pH dependent; changes in pH cause changes in the sorption efficiency of biomass [287]. pH also affects the solution chemistry of metal ions. In aqueous solution, metal ions (\(\text{M}^{2+}\)) undergo solvation, hydrolysis and polymerization [309–311] as indicated in the equations below:

\[
\begin{align*}
\text{M}^{2+} + n\text{H}_2\text{O} & \rightarrow \text{M(H}_2\text{O)}_{2n}^{2+} \\
\text{M(H}_2\text{O)}_{2n}^{2+} & \rightarrow \text{M(H}_2\text{O)}^{n-1}\text{(OH)}^+ + \text{H}^+ \\
n\text{M}^{2+} + n\text{H}_2\text{O} & \rightarrow \text{M}_n\text{(OH)}_{(2n-m)+} + m\text{H}^+
\end{align*}
\]

Most of the metal cations exist as free ions (\(\text{M}^{2+}\)) at a pH range of 2–5, but as the pH increases (>2), the positively charged metal cations quickly approach the negatively charged adsorbent surface. With further increase in solution pH, reactions between metal ions with these OH- ions results in the precipitation of metal hydroxides. This phenomenon also impacts the biomass sorption performance.

When the influence of pH on Ni loading onto beechwood was studied, the findings revealed that metal loading increased with increasing pH of the solution [278]. Because nickel hydroxide formation occurs at pH > 7 and wood chips have a pH_{ZPC} (6.7), optimum pH conditions of 6–7 were chosen to attain a high dispersion of nickel cations into the wood biomass matrix. Nickel-loaded biomass pyrolysis resulted in well dispersed Ni\(^0\) nanoparticles of 2–4 nm in the carbon matrix. The findings also suggested that both the initial nickel loading and final pyrolysis temperature influenced the crystallite size of Ni\(^0\), and these in situ generated NPs enhanced both tar conversion and \(\text{H}_2\) production. Addressing the effect of precursor metal salts, another study loaded Fe and Ni nitrates onto oak sawdust biomass and evaluated the catalytic effect of the metals [304]. Higher \(\text{H}_2\) yields were observed for Ni-laden biomass samples than for Fe-loaded biomass, whereas the latter reduced the production of gases. Similar findings were also reported for nickel-loaded biomass, for which higher levels of hydrogen was produced than for iron-loaded biomass, despite the higher char yield of iron-loaded biomass [306]. The effect of atmospheric pressure and vacuum impregnation on nickel adsorption onto beech wood has been explored [282]. Furthermore, the catalytic effect of NPs has been evaluated by inserting Ni\(^0\) NPs into biomass prior to pyrolysis. One interesting finding was that under atmospheric impregnation, Ni\(^2+\) adsorption onto biomass involved outer-sphere complexion, whereas under vacuum impregnation it involved inner-sphere complexion. The improved Ni insertion achieved under vacuum impregnation was due to inner-sphere complexion, and a higher catalytic efficiency was
observed for \textit{in situ} generated Ni\textsuperscript{2+} NPs as compared to Ni\textsuperscript{3+} NPs when each was inserted into biomass before pyrolysis. The effect of boron addition was examined in a study of nickel-impregnated rice husk (RH) biomass modified with sodium borohydride [284]. The results revealed that the addition of NaBH\textsubscript{4} encouraged the generation of Ni\textsuperscript{2+} NPs by deoxidizing NiO into metallic Ni\textsuperscript{2+} NPs, and also enhanced tar conversion during pyrolysis. Nanda et al. [312] used hydrothermal gasification to study the influence of temperature conditions, biomass-to-water ratios, and residence time on nickel-impregnated pinewood and wheat straw biomasses. Nickel impregnation onto biomass was carried out at pH 7–8 for quick sorption. Compared with non-catalytic gasification, higher yields of gas, hydrogen with superior carbon gasification efficiency was observed for nickel-impregnated biomasses.

Recently, composite materials comprising two unique constituents have gained particular attention in areas such as catalysis, water treatment, and biological applications. Among all composites developed to date, carbon composites made up of metal nanoparticles or magnetic particles have been used widely in water treatment due to their high surface area and magnetic characteristics, which facilitates high sorption efficiency and facile recovery [41,42,81,92]. CEMNPs have shown high sorption capacity and faster removal rates for inorganics compared with traditional activated carbon [269,313]. Nitric acid-treated CEMNPs have shown to have a high sorption capacity, i.e. 91.0 mg/g for Cd(II) compared with CNTs (20.37 mg/g) and AC (9.91 mg/g) [314]. Considering the high sorption performance of CEMNPs, several attempts were made to treat various pollutants in one study, porous carbon sheets containing carbon-encapsulated Fe\textsubscript{3}Fe\textsubscript{4}C (Fe\textsubscript{3}Fe\textsubscript{4}C@PCS) were fabricated using gelatin biomass and Fe(NO\textsubscript{3})\textsubscript{3}·9 H\textsubscript{2}O as precursors [315]. The material successfully removed uranium from aqueous medium via surface adsorption and led to \textit{in situ} reduction of U(VI) into U(IV). Comparisons were made between the sorption efficiencies of activated carbon and Fe\textsubscript{3}Fe\textsubscript{4}C@PCS for U(VI), and activated carbon (AC) had a limited sorption performance that was effective at low initial concentrations due to the limited active sites of AC. Whereas, even at high concentrations of up to 140 mg/L, Fe\textsubscript{3}Fe\textsubscript{4}C@PCS was effective for U(VI) removal (~100%). In another approach, agar was used as the biomass precursor, along with Fe(NO\textsubscript{3})\textsubscript{3}·9 H\textsubscript{2}O and Al(NO\textsubscript{3})\textsubscript{3}·9 H\textsubscript{2}O as metal precursors, to manufacture porous carbon sheets containing carbon-stabilized Fe\textsubscript{3}Fe\textsubscript{4}C nanoparticles [275]. The material exhibited a high surface area of 1023 m\textsuperscript{2}/g and successfully adsorbed the organic pollutants methylene blue, methyl orange, and crystal violet with sorption capacities of 1616, 1062, and 1728 mg/g, respectively. These materials have the added advantage that they can be easily removed from aqueous solutions due to their magnetic properties, unlike other materials.

Cu NP (average particle size of 21.2 nm) anchored magnetic carbon (Cu and Fe\textsubscript{3}O\textsubscript{4}-nc) was manufactured by fast pyrolysis of Fe/Cu adsorbed fir sawdust biomass and the material was used as a catalyst for the catalytic reduction of 4-nitrophenol [316]. When the performance of Cu and Fe\textsubscript{3}O\textsubscript{4}-nc was compared to that of magnetic carbon, the Cu and Fe\textsubscript{3}O\textsubscript{4}-nc showed more effective catalytic reduction of 4-nitrophenol, likely due to the presence of Cu nanoparticles, which have exceptional catalytic properties. This catalyst retained 95% of its reduction efficiency after 5 cycles, suggesting that it is effectively recyclable. Release of the heavy metal Cu throughout the 5 cycles was measured to determine the risk of toxicity to aquatic environments, and was found to be <1.0 mg/L, which is below surface water limits. In another study, compressed carbon black was used to manufacture C-Fe\textsubscript{3} particles using adsorption and impregnation procedures, and the resulting materials were tested for Cr(VI) remediation [317]. The results revealed that the BET surface area of C-Fe\textsubscript{3} particles that were prepared through adsorption was higher (130 m\textsuperscript{2}/g) than that of the starting carbon material (80 m\textsuperscript{2}/g). The presence of C-Fe\textsubscript{3} reduced the Cr(VI) concentration from 10 to ~1 ppm.

Most of the studies described above focus on metal-loaded biomass, but dye loaded adsorbents have also been used to manufacture nanoparticles by adding the appropriate metal ion precursor to the post-sorbed. Tian \textit{et al}. [98] used an interesting strategy to prepare a multifunctional nanocomposite, which was to combine AgNO\textsubscript{3} and methyl violet-loaded palygorskite in a hydrothermal process. The dye adsorbed onto the palygorskite acted as carbon source, whereas the Ag(I) promoted carbonization of the dye molecule. This composite exhibited good sorption efficiency for methylene blue (99.2%), methyl violet (86.9%), chlortetracycline hydrochloride (68.7%), and tetracycline (46.2%). It also exhibited good catalytic properties by reducing 4-nitrophenol to 4-aminophenol with good reusability (8 cycles). A summary of adsorbents and metal ion precursors used in the fabrication of carbon-nanoparticles is given in Table 3.

Biosorption, the sorption of metal ions from various biomaterial wastes, has been one of the more highly studied topics due to its effective removal of various metal ions from aqueous solutions. However, researchers are still looking for alternative strategies for the safe disposal of spent or metal-loaded biosorbents. Post-sorbed metal ions on biomass could be utilized as feedstock for harvesting nanoparticles in a carbon matrix through modern pyrolysis processes. Several factors that influence the sorption ability of biomass include pH, temperature, vacuum/ambient, biomass characteristics, and type of metal salts (e.g. nitrate, chlorides, etc.). One of the key factors that influences the harvesting of nanoparticles is the pH of the solution during impregnation [318]. pH is always controlled, because the optimum sorption of metal ions occurs when metal ions are well dispersed and in high amounts on the biomass. This ideal method will provide an opportunity to manufacture value-added products such as: (i) syngas, (ii) nanoparticles, (iii) biochar, (iv) reusable catalysts, and (v) resource recovery. The cost of raw materials influences the overall cost of any technology, and for \textit{in situ} generation of nanoparticles, the cost of metal ion precursors is significant. Due to its good catalytic activity, nickel is one of the most widely used precursors for harvesting nanoparticles. Electroplating wastewater is rich in nickel ions and can be used for loading nickel ions into a biomass matrix [284,319]. In addition to metal-containing wastewaters, seawater, which is rich in metal ions [320], is also useful and, because it is an inexpensive resource, the overall cost of carbon-nanoparticles synthesis would be reduced. For example, in one study, seawater-rich MgCl\textsubscript{2} was used as a precursor along with sawdust biomass for manufacturing mesoporous carbon stabilized MgO nanoparticles, and the resulting material was successfully used for CO\textsubscript{2} capture [234].

Although CEMNPs have a wide range of applications in diverse fields, there are several limitations. Ni-based catalysts are often used to prepare CEMNPs because of their enhanced catalytic activity and reduced cost. However, Ni-based catalysts are less stable and further prone to coke development [284,321]. Uniform distribution of metal ions in the biomass is required. Alternatively, carbon formation without metal nanoparticles is possible, and in the case of water treatment, it is hard to separate the fine carbon powder. Fabrication of these materials requires technologically advanced instruments and high temperatures. For producing CEMNPs both precursor biomass and metal ions should be obtained at low cost (i.e. in the form of waste); otherwise, the overall fabrication cost of CEMNPs will be higher. In recent years, the toxicity of emerging materials has come into question. In the case of CEMNPs, although nanoparticles are covered with a carbon shell that protects them from direct contact with biological fluids, environment toxicity of CEMNPs is off under scrutiny [272]. The results revealed that the cytotoxic response to these particles depends on their physicochemical characteristics, specifically surface characteristics [272,322–324].

2.3. Feed additives

Trace elements, also known as trace minerals (dietary minerals), are essential inorganic feed additives that provide the key nutrients required for various metabolic functions in living organisms. These are required in tiny quantities for proper growth and development, and play a vital biological role in nerve transmission, hormones, energy production, blood sugar levels, metabolism, digestion, and cholesterol [329].
Of the 90 elements that occur naturally, approximately 26 are considered to be essential for mammalian life, and some of these include: B, Co, Cu, F, Fe, I, Li, Mn, Mo, Ni, Se, Si, V, and Zn, and possibly As, Cr, and Sn [330–333]. Although all of these elements are involved in biological functions, the trace elements required for good health are copper, cobalt, iron, iodine, manganese, molybdenum, selenium, and zinc [334–338]. Deficiencies of these minor trace elements can adversely affect the health of both animals and humans, leads to chronic illnesses such as anemia, diabetes, Alzheimer's disease, aging, hypertension, fertility issues, and reduced immune system function [339–342]. As an example, Zn is one of the essential micronutrients required for normal growth and development [343,344]; however, it is estimated that 17% of the global population is at risk of Zn deficiency due to low dietary Zn intake [345].

Certain trace mineral insufficiencies in livestock can be classified as either primary or secondary deficiencies. A primary deficiency occurs as a result of a diet that is low in one or more trace minerals, while a secondary deficiency results when there is reduced nutrient absorption due to either enhanced metabolism or secretion of a specific nutrient [346,347]. When an animal suffers from mineral deficiencies due to lack of trace elements, the meat or milk produced by those animals also contains inadequate levels of these trace elements. Consumption of products from mineral deficient animals results in a similar deficiency in humans [348]. As an example of successful reversal of this effect, in the United Kingdom, cases of iodine(I) deficiency in humans decreased after iodine supplementation of dairy cows, presumably because iodine progresses into cow's milk, which is then ingested by humans [349]. Animals with mineral insufficiency might not exhibit any outward symptoms, however, they may have reduced performance potential and less than ideal health conditions. It is also possible to ingest excessive amounts, however, they may have reduced performance potential and less than ideal health conditions. It is also possible to ingest excessive levels of trace minerals naturally or through diet supplementation, and this too has a negative effect on health, leading to acute toxicity problems and possibly induction of deficiencies in other related trace minerals [333,336,350]. Scientific studies have carefully defined the nutritional needs of animals, and designed feed formulations containing appropriate levels of micronutrients to support the efficiency of animal husbandry and food production. Ideally, eatable animal foodstuffs (meat, eggs, dairy products, etc.) should contain quantities of trace minerals that are optimal for ensuring human health. To handle micronutrients as precisely as possible, premix and feed producers rely on sources of trace minerals that have ideal physical and technological properties. For instance, copper and zinc are critical trace minerals that improve production and reproduction in farm animals [351]. However, the form of the food, organic or inorganic, makes a difference in the availability of these minerals to the animal, because inorganic forms of trace minerals are not adequately absorbed and retained [351]. In contrast, organic forms are absorbed well and are maintained in tissues, improving performance, immunity, health, and reproduction of the animals [352].

Biosorption technology, which enables sorption of a broad range of metal ions, is one of the best methods of manufacturing fine-tuned trace mineral supplements. Trace minerals can be loaded onto the inexpensive, edible, and abundant biomass, and the resulting feed can be used in animal husbandry. Several researchers have focused on developing feed supplements that make use of biomass-based sorbents. In particular, Prof. Katarzyna Chojnacka’s group in Poland has been one of the most successful teams, making valuable progress in this research area and bringing this technology from the laboratory to pilot scale manufacturing [353–355]. This research group had promising results with a broad range of trace metal-enriched biosorbents used as feed additives. They have published an excellent review on manufacturing agrochemicals, including a discussion of the application of metal-enriched biosorbents for feed supplements [356].

Seaweed biomass, macroalgae, soybean meal, and spent mushroom have been used as substrates to adsorb metal ions, and were studied for their subsequent influence on animal performance (meat, milk and eggs). Because both Zn(II) and Cu(II) are important for animal growth, the effectiveness of a biosorbent made from macroalgae Enteromorpha sp. enriched with these two trace elements was studied for effectiveness as pig feed [357]. For comparison, inorganic salts were fed to a control group. A mineral composition analysis of the meat frompigs in control and experimental groups revealed that experimental group had a significant increase in the concentration of the trace mineral.

Table 3

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Metal precursor</th>
<th>Temperature/atmosphere</th>
<th>Post adsorbent characterization and applications</th>
<th>Efficiency</th>
<th>References</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td>NPs (size nm)</td>
<td>Surface area</td>
<td>Application</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ni (NO3)2·6 H2O</td>
<td>NiO</td>
<td></td>
</tr>
<tr>
<td>Agar</td>
<td>Fe/Al</td>
<td>800 °C/N2</td>
<td>Fe/Fe2C</td>
<td>1023</td>
<td>Dye removal</td>
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<td></td>
<td></td>
<td></td>
<td>Ni (NO3)2·6 H2O</td>
<td>Fe/Fe2C</td>
<td>95.9</td>
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<tr>
<td>Beech wood gelatin</td>
<td>Fe</td>
<td>700 °C</td>
<td>NiO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beech wood chips</td>
<td>Ni (NO3)2·6 H2O</td>
<td>700 °C (5 °C/min)</td>
<td>NiO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sawdust</td>
<td>MgCl2·6H2O</td>
<td>773–973 K/N2</td>
<td>MgO</td>
<td>186</td>
<td>Acid catalyst (benzyl acetate)</td>
</tr>
<tr>
<td>Sawdust</td>
<td>Cu(NO3)2·6H2O</td>
<td>773 K/N2</td>
<td>CuFe2O4</td>
<td>296</td>
<td>4-Nitrophenol reduction</td>
</tr>
<tr>
<td>Rice husk</td>
<td>Ni (NO3)2·6 H2O</td>
<td>750 °C/N2</td>
<td>NiO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beechwood chips</td>
<td>Ni (NO3)2·6 H2O</td>
<td>700 °C (5 °C/min)</td>
<td>NiO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pinewood &amp; wheat straw</td>
<td>Ni (NO3)2·6 H2O</td>
<td>750 °C/garbon (10 °C/min)</td>
<td>NiO</td>
<td></td>
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<tr>
<td>Beech wood-chips</td>
<td>Ni (NO3)2·6 H2O</td>
<td>850 °C/N2</td>
<td>NiO</td>
<td>465</td>
<td>H2 production</td>
</tr>
<tr>
<td>Rice husk char</td>
<td>Fe(NO3)3·9H2O &amp; Ni(NO3)2·6H2O</td>
<td>600 °C</td>
<td>Ni-Fe</td>
<td>92.3%</td>
<td>-</td>
</tr>
<tr>
<td>Rice husk</td>
<td>Ni (NO3)2·6 H2O</td>
<td>~700 °C/N2</td>
<td>NiO</td>
<td>135</td>
<td>H2 production</td>
</tr>
<tr>
<td>Pinewood</td>
<td>Ni (NO3)2·6 H2O</td>
<td>-</td>
<td>Ni (&lt;100)</td>
<td>-</td>
<td>Gas and H2 yields</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>Ni (NO3)2·6 H2O</td>
<td>-</td>
<td>Ni (&lt;100)</td>
<td>-</td>
<td>Gas and H2 yields</td>
</tr>
<tr>
<td>Compressed carbon black</td>
<td>Fe(NO3)3·9H2O</td>
<td>800 °C/Ar</td>
<td>Fe3O4 (20 to 150 nm)</td>
<td>130</td>
<td>Cr(VI) remediation</td>
</tr>
<tr>
<td>Palygorskite</td>
<td>AgNO3</td>
<td>180 °C/autoclave</td>
<td>Ag</td>
<td>205</td>
<td>Sorption/catalysis</td>
</tr>
</tbody>
</table>
significantly higher level of Mn (49%) than the control group. In other studies, microalgal biomass comprised of *Spirulina maxima* was utilized as a feed supplement for swine and laying hens after enriching it with the metal ions Cu(II) and Fe(II) [358,359]. In experiments on laying hens, it was observed that the trace minerals Fe(II), Zn(II), and Mn(II) were present at higher levels in the egg albumin of the experimental groups as compared to the control groups [359]. A pilot plant arrangement was also used to manufacture Zn(II), Cu(II), Mn(II) and Fe(II)-enriched soybean meal using sorption technology and the post-sorption material enriched with metal ions was used for zootechnical tests [355]. The nutritional content of feed containing these adsorbents and their applications of each are summarized in Table 4.

A wide variety of sorbents can be useful for manufacturing nutrient enriched feed; however, biomass substrate has often been chosen for this purpose. Although no studies have reported the application of nutrient-loaded zeolite (sorption-based) as feed supplements, zeolites should be considered for this purpose. Use of zeolites themselves as feed additive has been reported, and has been accepted by various regulatory agencies. For example, both the U.S. FDA and the EU have approved clinoptilolite as a feed additive [230]. An in vitro study evaluating the effect of zeolite on the gastrointestinal tracts of swine found no signs of toxicity [360]. The release of extremely low concentrations of Pb and other toxic elements was observed; however, the concentration of Pb was well below the limits allowed by European Regulations (E566). Prasai et al. [361] studied the effects of feed supplements containing biochar, zeolite, and bentonite on layer chickens and the findings revealed that these feed additives are effective in controlling zoonotic pathogens. Several studies have reported that zeolites not only influence disease resistance, but also have a positive effect on immunological and hematological factors [362]. Natural zeolites are microporous crystalline, hydrated aluminosilicates of alkali and alkaline earth cations that have unique physicochemical characteristics including ion-exchange and adsorption-desorption abilities. A wide variety of natural and synthetic zeolites have been used for wastewater treatment, effectively removing metal ions such as copper, zinc, manganese, and boron [82,363–367]. Further studies are needed in order to recognize the full potential of trace element-enriched zeolite and its application in feed supplementation.

Most of this research has focused on enriching sorbents with various trace elements and using this as a supplement to animal feed. However, vitamins and antibiotics are also essential to the performance of livestock and prevention of disease. For example, pharmaceuticals are often used in farm animals for both therapeutic and prophylactic purposes, and are distributed through feed or drinking water [368]. Thus, sorption-based technology could be useful in the development of drugs and/or vitamin-loaded feed supplements as well. Several researchers have reported that sorption technology has enabled the successful removal/recovery of various drugs [369–374]. Thus, biomass used to feed animals could be tailored with particular drugs/vitamins, and should be considered as a method for manufacturing feed supplements (Fig. 10). Among the metal ions, because Fe, I, Zn, Ca, Mg, Cu and Se are often deficient in the human diet, these specific elements are worth considering when manufacturing feed-additives [135].

Several challenges still exist when feed supplements are manufactured through biosorption technology, the greatest of which is ensuring that the optimal concentration of trace elements is achieved. Before feed can be manufactured, the precise deficiency and sufficiency levels of the diet for each type of animal must be defined [350]. Even though most studies have focused on enrichment with a single trace element, clearly it is essential to develop techniques to manufacture multi-mineral nutrients to meet complex nutrient demands. Additionally, emission of ammonia from manure is a significant environmental challenges faced by the poultry industry. Supplementation dietary trace minerals (eg. zinc) may be one solution, because this supplementation leads to reduction in both nitrogen excretion and emission. In addition, mineral supplementation inhibits microbial uricase activity, which there by decreases the production of ammonia [375]. Supplementing with zeolite could be particular useful as it has a high selectivity for ammonia [230]. Farming strategies can be developed to include custom tailored post-sorbert that is rich in the specific trace elements or a combination of elements needed for each particular type of animal. Moreover, it is also essential to identify the sorbate (trace mineral)-sorbert (biosorbent) interactions and the particular metal complexation form. It is conceivable to regulate this supplementation and to determine the metal-releasing performance for each. Analytical determination of metal toxins in animal feed is often challenging due to the complexity of the feed matrices and extremely low concentrations of metal ions. This should be considered as an important issue in manufacturing feed-additives. One of the major problems with feed additive use is that, as in humans, elevated levels of particular elements can lead to acute health problems in animals. Furthermore, consumption of the food materials (meat, eggs, milk, and dairy products) derived from these animals may subsequently severely affect human health. Thus, the safety and toxicity of feed supplements should be thoroughly assessed prior to their application, and supplementation should be carefully controlled with particular care taken to measure any toxic effects of trace elements that may be present in high quantities. Some biomass feedstocks contain potentially toxic elements, such as Pb, Cd, Hg, and As, that are harmful to both animals and humans [376]. For instance, toxic effects of organic arsenical compounds that have been widely used in poultry feed have been well documented [377–379], and inorganic arsenic has been found in both meat and manure [378,380]. Yao et al. [381] reported the quantitative delivery of roxarsone via a chicken diet to rice plants and their subsequent environmental and health issues. Thus, before biosorbent feed is utilized, a complete elemental composition analysis should be carried out. Global meat consumption has increased dramatically, and it has been estimated that the demand for animal-derived products and meat will continue to grow in the coming decades [382,383]. Meat is an excellent carrier of trace elements, and provides these in an organic form [384,385]. Thus, enrichment of meat with supplements as a means of transferring essential elements to humans via the food-chain is worthy of investigation.

Several international regulations address the impact of trace minerals on living organisms, providing stringent regulations on maximum supplementation levels [386]. The European Union, according to the Commission Regulations (EC) 1334/2003, has reduced the recommended trace element levels in animal feed in recent years to address the importance of food safety and the environment [387]. In the EU, animals intended for slaughter are permitted to have maximal levels of cobalt, copper, iron, iodine, manganese, selenium, and zinc in feed at 2, 25–35, 750, 10, 150, 05 and 150 mg/Kg, respectively [383,388]. Furthermore, the toxic effects of certain metals, such as chromium, vary with oxidation states, so this should be taken into consideration [389,390]. The use of organic arsenical compounds in the broiler chicken industry as feed-additives was well-known; however, because of toxic effects, the US FDA banned arsenic, carbarsone, and roxarsone in 2013 [391]. Antibiotics used to boost the growth of farm animals are now being regulated, and no trace of the parent compound or its metabolites may remain in food products, as per the European Union feed additive legislation (Council Directives 70/524/EEC and 96/51/EC) [392]. Milk, cheese, meat, and eggs are a major food source. Because levels of trace minerals in these animals exist in their animal products, careful study and regulation is needed when manufacturing trace mineral laden sorbents (feed-additives), and when screening the produced materials to avoid food toxicity and environmental pollution.

Although it seems there is a large scope available for the development of commercial feed additives through sorption-based technology still several limitations exists. Feed safety is most vital norm as the material used for animal feed should not be a threat to either animal or human health and also to environment. Another key limitations in post-sorbert based feed- additives is the sorbed element should not
exceed the maximum concentration levels if it will causes damage to the animal and human health. In such case caution is required to dispose the manufactured feed safely otherwise it will contaminate the environment. Besides some of the biomass-based materials used as sorbents are complex matrix that contains wide variety of elements and natural products thus complete sorbent analysis is essential. Loading of pharmaceuticals is needed additional care as it is well-known that pharmaceuticals undergo transformation depends on the environment, thus careful residual analysis is required to determine the presence of original drug or its metabolite residues in the animal meat or their excretions. Thus it is essential to carefully analyze the animal products to identify the presence of any harmful pharmaceutical by-products. Further research is required to study the risk assessment of post-sorbent based feed additives. Another significant limitation is cost of the feed manufactured through sorption-based technology should not exceed the available feed costs.

### 2.4. Catalysts

Catalysis is a key step that can be modified when developing the sustainable practices necessary to produce chemical compounds [396]. Heterogeneous catalysis is an effective technique that involves the fabrication of a stable catalyst on a solid support [397]. The use of metal catalysts, such as Ni, Ru, and Pd, on a homogenous solid catalyst support enhances the catalytic activity [398–401]. Solid supports have often been required to prepare highly dispersed metal catalysts, and they have several advantages, including recovery, regeneration, and reuse [402]. Adsorption has been used to adhere metal ions onto solid adsorbents, and post-sorbents containing metal ions have catalytic oxidation properties that may be useful in the treatment of organic contaminants. In recent years, there has been much interest in reusable catalysts, which can be easily separated and easy to recover, and magnetic and reusable catalysts are of particular interest. Magnetic adsorbents have been widely used for water treatment, and these may exhibit exceptional sorption capacity towards various metal ions. These metal-loaded magnetic sorbents can be efficiently used as catalysts, and therefore there have been several attempts at this application.

Post-sorbents that have been loaded with metal ions have also been utilized as catalysts for the degradation of various toxic pollutants. Wu et al. [403] manufactured nickel-sorbed porous graphene oxide/sawdust composite (NiO@GNCC), and the post-sorbent was reduced by NaBH4 to create a catalyst that was useful in the degradation of phenol in aqueous solutions. A high sorption capacity of 158.98 mg/g for phenol was accomplished using NiO@GNCC; however, the reusability and stability of the catalyst was not studied. Biomass, such as fly ash and sawdust, has been used to recover nickel ions from wastewater, and the post-adsorbent was reused for the degradation of 2-chlorophenol [404]. Prior to its use as catalyst, the post-adsorbent was dried, blended, and calcined. Improved surface area, which plays a key role in the catalytic activity, was observed for the catalyst when compared with fly ash. If sawdust, which is naturally abundant, has been used to preload Ni(II)/Fe(III), and then the sorbed biomass was pyrolyzed to obtain Ni-NiFe2O4/CNF catalyst [405]. Fast pyrolysis of metal preloaded biomass resulted in magnetic NiFe2O4, Ni(0) nanoparticles, and carbon nanofibers. This manufactured catalyst exhibited good performance in the hydrogenation of aromatic nitrobenzene to aniline without any

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**Table 4** Sorption based feed additives (nutrient-loaded adsorbents) and their characteristics.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Micronutrient</th>
<th>Content of microelement in feed</th>
<th>Post-sorption applications</th>
<th>Estimated nutrient after feeding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soya bean meal</td>
<td>Cu(II)</td>
<td>11.7 ± 1.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Goats/14 days</td>
<td>8.2% (milk)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Mn(II)</td>
<td>5.92 ± 0.77&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td>29.2% (milk)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Zn(II)</td>
<td>0.06 ± 1.18&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td>14.6% (milk)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Fe(II)</td>
<td>11.9 ± 1.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td>–</td>
</tr>
<tr>
<td>Macroalga Enteromorpha sp.</td>
<td>Zn(II)</td>
<td>56.4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Pig/3 months</td>
<td>Zn, &gt;9.5% (blood)&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>Spirulina maxima</td>
<td>Cu(II)</td>
<td>51.6&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Pig/87 days</td>
<td>18.3% (meat)&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>Soya bean meal</td>
<td>Cu(II)</td>
<td>11.7 ± 1.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Pig/91 days</td>
<td>10.4% (Loin)&lt;sup&gt;b&lt;/sup&gt;</td>
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<td></td>
<td>Fe(II)</td>
<td>11.9 ± 1.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td>20.4% (Loin)&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td></td>
<td>Mn(II)</td>
<td>5.92 ± 0.77&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>9.0% (Loin)&lt;sup&gt;b&lt;/sup&gt;</td>
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<td></td>
<td>Zn(II)</td>
<td>9.06 ± 1.18&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>7.8% (Loin)&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>Soya bean meal</td>
<td>Cu(II)</td>
<td>15.690 ± 0.370&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Laying hens</td>
<td>–</td>
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<td></td>
<td>Zn(II)</td>
<td>14.088 ± 0.403&lt;sup&gt;a&lt;/sup&gt;</td>
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<td></td>
<td>Fe(II)</td>
<td>16.337 ± 0.228&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td></td>
<td>Cr(III)</td>
<td>20.588 ± 0.212&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>Macroalgae</td>
<td>Cu(II), Zn(II), Mo(II), Co(II), Cr(III)</td>
<td>–</td>
<td>Laying hens</td>
<td>Cu-56%, Zn-171%, Cr-723% (egg white)&lt;sup&gt;b&lt;/sup&gt;</td>
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</table>

<sup>a</sup> mg/g.
<sup>b</sup> Percentage increase compared with control.
<sup>c</sup> g/kg.
detectable azobenzene or azoxybenzene byproducts. This catalyst also showed good reusability, in that there was no significant decrease in aniline yield after 7 cycles. High aniline yield (~100%) was accomplished with Ni-NiFe₂O₄/CNF, whereas individual Ni NPs, NiFe₂O₄, and CNF exhibited yields as low as 53%, 29%, and 14%, respectively. Most of the sorption studies focused on the removal of single metal pollutant even though wastewater often consists of a mixture of both cationic and anionic metal ions. Considering this, an attempt has been made to remove both cationic (Cu²⁺) and anionic (CrO⁴²⁻) pollutants using a layered double hydroxide adsorbent [406]. This adsorbent is useful for treating both types of metal ions due to the synergetic effect between both Cu and Cr ions during sorption process. Further spent Cu/Cr loaded sorbent has been used as a catalyst for MO degradation. The catalytic activity of sorbent, Cu loaded sorbent, Cr loaded sorbent, and Cu/Cr loaded sorbent were evaluated, and it was found that Cu/Cr-loaded spent sorbent was most effective and showed the highest level of degradation (86.5%). In another approach, bacterial biomass was used as precursor to manufacture biomass-Pd catalyst and the catalytic efficiency for Cr(VI) reduction was found to be 90% after 30 min for both bioPd₆. desulfuricans and bioPdE. coli [407]. Catalysts manufactured through the retrieval of metal ions from aqueous solutions were also used for oxidation of air pollutants, including volatile organic compounds. In one study, Cr(VI)-loaded Arthrobacter viscosus supported on NaY zeolite was obtained through sorption experiments [408]. The manufactured materials were calcined at 400 °C in air flow and the prepared catalyst was used for the oxidation of ethyl acetate, ethanol, and toluene in the following sequence: ethanol > ethyl acetate > toluene. Similarly Cr-loaded sorbents have been used as catalysts for the oxidation of 1,2-dichlorobenzene [409] and cyclohexene [410]. These studies suggest that spent sorbents can be used as efficient catalysts for the degradation of organic compounds and, in addition, most were easy to separate after the catalytic process was complete.

Although post-sorbents have been shown to have good catalytic performance, there are still a few limitations that hinder their practical applications. Most of the sorbent materials are prepared from expensive raw materials and through complex synthetic routes to enhance the overall catalytic process. The focus should be on the fabrication of economical catalysts that utilizing low-cost biomass waste (sorbent) materials and metal (sorbate) contained in wastewater through facile synthetic routes. In addition to the studies on a laboratory scale, further pilot-scale studies are going to be required to increase this technology to an industrial scale. A major limitation on practicality of this approach is the presence of toxic metal ions and nanoparticles in the post-sorbent, because these may be released into the environment both during catalytic processing and after use (storage and landfills). Evidence of leaching of toxic metal ions and nanoparticles fromadsorbents and catalyts has been well reported [81,411]. Leaching of metal ions causes the generation of M⁰⁺ ions, and occasionnally, the development of nanoparticles. Among the various metal ions used in catalysis, nickel and copper are often considered to be sustainable and non-toxic. However, Egorova and ananikov [411] have described these metal ions as toxic. Safe storage or disposal of the spent catalysts containing metals or nanoparticles is of high concern due to stringent environmental legislations. For instance, the US EPA classified spent catalysts as hazardous waste because of the existence of the considerable amount of heavy metal ions [412]. To overcome this limitation, it is feasible to fabricate Ca-based catalyts, made by loading Ca onto adsorbnts that are non-toxic and economical [413].

2.5. Bioactive compounds

In addition to the applications described thus far, metal-loaded sorbents have been shown to be useful for other functions, including biological activity. Most of the post-sorbents exhibit disinfection properties and other shielding biological effects. These biological effects have been attributed to the constituent metal ions, particularly Cu, Zn, and Mn. As a result of these observations, post-sorbents have been evaluated to determine their usefulness in antimicrobial and antioxidant applications, and here we summarize those that have shown interesting biological effects.

Knowing that silver is a potent antimicrobial, biochar loaded with Ag⁺ was evaluated for its antimicrobial ability and found to efficiently inhibit the growth of Escherichia coli, whereas biochar without silver had the opposite effect and promoted the growth of Escherichia coli [414]. In another study, chitosan/nano Al₂O₃ loaded with Cu(II), a known antibacterial, exhibited good antimicrobial activity against E. coli when compared to chitosan and chitosan/nano Al₂O₃ alone [415]. The adsorbent was also used for removal of As(III) with a sorption potential of 18.32 mg/g at pH 7. Bioactive ceramic hydroxyapatite [Ca₁₀(PO₄)₆(OH)₂] was used to retrieve chlorhexidine digluconate through an adsorption process, and the post-sorbent inhibited Enterococcus faecalis growth in vitro for up to 6 days [416]. Serbian clinoptilolite was used for the adsorption of Zn(II) and exhibited a maximum sorption capacity of 16.8 mg/g [417]. In the presence of air, the post-sorbent was thermally treated at 540 °C to produce ZnO-clinoptilolite. Both materials, Zn-clinoptilolite and ZnO-clinoptilolite, were tested against Acinetobacter junii, and the former exhibited good antibacterial activity. Four different algal biomass powders loaded with zinc, copper and silver through sorption equilibrium were tested for their antimicrobial properties against Escherichia coli [418]. Algae loaded with Ag had a stronger bacterial effect than Zn-loaded algae or algae alone. The microalgae Chlorella vulgaris loaded with polyphenols was evaluated based on antioxidant activity, and biomass enriched with quercetin had the highest antioxidant activity [419]. These interesting findings suggest that post-sorbents containing bioactive metal ions, particularly Ag, Cu, and Zn, can be employed as antibacterial, antifungal, and antioxidant agents. Although such post-sorbents have been shown to have antimicrobial activities, further research is required to assess the biocompatibility and toxicity of these materials of these post-sorbents in various applications.

2.6. Miscellaneous applications

Besides the applications described above, few studies have explored the recovery of adsorbate after post-sorption. Due to the cost of critical metals and their resource limitations, several studies have focused on the recovery of metal ions from post-sorbents using incineration or pyrolysis techniques [420–424]. Bark species were used in one study for the removal of copper and incinerated in the presence of air and nitrogen [420]. A thermogravimetric and X-ray powder diffraction (XRD) analysis of incinerated ashes indicated that CuO (~80%) and Cu²⁺ (~14%) were present in the produced solid. In another study, olive solid waste generated from an olive oil mill was used for copper and nickel sorption, and accomplished a sorption capacity of 3.6 and 1.7 mg/g for copper and nickel, respectively [421]. Metal-loaded biosorbt was burned at 850 °C in an oven and the resulting ashes contained 96% of each metal. Desorption is the most commonly used conventional process for the recovery of sorbate from adsorbent, however, this process requires a large amount of desorbing agent. This will invariably increase the cost of sorption-based technology, and secondary pollution is a possible consequence of this approach. Liu et al. [425] made an attempt to understand the technical and economic feasibility of biosorption-pyrolysis technology as compared to biosorption-desorption process when used for lead recovery. The results demonstrated that biosorption-pyrolysis technology, which costs $0.06 per ton of wastewater, is more beneficial when compared to a biosorption-leaching process, which costs $0.19 for HCl and $ 4.41 for EDTA per ton of wastewater. Considering the importance of precious metal ions in a wide variety of applications and their resource limitations, our group investigated gold and ruthenium recovery after post-sorbent incineration [422,423]. We successfully recovered 59.75% of Ru and ~91% of gold through a sorption-incineration approach. In
another study, the precious metal platinum was recovered using an amine modified corn husk, followed by calcination of the post-sorbent at 800 °C for 12 h [426]. The results revealed that 54% of the calcined powder was platinum.

Dye-loaded biosorbent has been used to manufacture biochar material [54]. Through a pyrolysis technique, dye-laden biosorbent was further converted into biochar, which was then used for methylene blue (MB) removal. Biochar showed good removal performance at lower initial MB concentration when compared to other common biosorbents. In another study, methylene blue loaded carboxymethyl cellulose was used for methylene orange (MO) removal, MB loaded CMC exhibited a high sorption efficiency of >100 mg/g for MO, and is much higher than the CMC sorption efficiency for MO [427]. Post-sorbents have also been used for fuel cell technology. In a fuel cell, yeast biomass loaded with Pt (PtCl62−) was used as an electro-catalytic anode to generate electricity from glucose and ethanol [428]. Additionally, metal-loaded adsorbent was used to obtain metal oxide nanoparticles; specifically, clinoptilolite was shown to remove Ni(II) ions from aqueous solutions. Thermal treatment of post-sorbent (Ni(II) loaded clinoptilolite) resulted in nano-sized NiO particles of ~5 nm [429].

Interestingly, only a few post-sorbent applications in energy production have been proposed [52,53,430]. Energy is one of the most vital 3E issues. It is a key factor in the economic development of all countries, since industries and individuals alike are highly dependent on energy supplies. The amount of available petroleum fuels is diminishing, and there is a lack of acceptance for nuclear energy [431–434]. To address these problems and meet the future energy demands of growing populations and increasing industrial activities, utilization of alternative energy resources, such as wind, tide, solar, geothermal, and biomass, is becoming more important [303]. Among these, bioenergy produced from biomass has become an alternative to fossil fuels, and it has great potential to provide a stable source of power. In the United States, the use of biomass-derived energy increased by 60% between 2002 and 2013 [435]. Even though this form of energy production is important, few studies have been conducted to evaluate the use of post-sorbents in power generation.

Converting biomass into valuable energy and chemical products through pyrolysis is one of the frontiers in thermochemical technology; this process results in gas (pyrolytic gas), liquid (bio-oil), and solid (biochar) [436–438]. Bio-oil and/or gas obtained through biomass pyrolysis can be used for energy production. Several researchers have made attempts to utilize the exhausted biosorbent (post-sorbent) to gain valuable resources through pyrolysis, combustion and gasification processes, while simultaneously reducing the volume of waste. However, biomass pyrolysis depends on parameters such as biomass pretreatment, heating rate, reaction atmosphere, temperature, and biomass source [439]. Exhausted or spent sorbent consists of metal ions, which influence the biomass pyrolysis process. Thus it is essential to evaluate the sorbate effect on pyrolysis process. As an example, pine cone shell biomass was used for Pb(II) and Cu(II) removal from aqueous solution in a packed bed column [52]. When the effect of Pb(II) and Cu(II) on thermal decomposition of the biosorbent was studied, revealing that these metals did not influence the major degradation pathways. Thermal decomposition of the metal-loaded biosorbent resulted in chars, with 95% and 99% recovery of copper and lead, respectively. Combustion of olive tree pruning biomass loaded with Pb(II) was studied in a thermobalance, a laboratory flow reactor and an atmospheric oven [53]. The total concentration of Pb(II) remains in the ashes suggesting that this does not influence the usage of biomass as fuel. However, if high amounts of Pb(II) (~35%) are present in ash, then further treatment or applications should be explored to mitigate the toxic effects of lead. Pine cone shells were used in one study to sorb copper from aqueous solution and a sorption capacity of 0.81 mg/g was achieved before the post-sorbent was thermally decomposed [430]. Both sorbent and post-sorbent exhibited similar pyrolysis and combustion behaviors, with major compounds being CO, CO2, CH4, C2H4, CH3OH, and SO2.

These studies suggest the feasibility of application of metal loaded sorbents for energy production.

3. Conclusions and future perspectives

Adsorption is one of the key techniques that has been used in separation science to retrieve various pollutants and analytes from the aqueous phase, and therefore, has attracted substantial interest for scientific and commercial applications over the past several decades. Due to the accessibility of widespread, naturally abundant adsorbent materials, as well as the emergence of new generation materials, much research has gone into exploring the use of these materials in water treatment applications. High sorption efficiencies, rapid removal rates, and selectivity are the chief properties to consider when designing adsorbents, whereas less attention has been paid to post-sorbent management or to possible further utilization of post-sorbents. In recent years, there has been an increasing level of interest in the development of sustainable technologies to minimize the cost of materials/techniques and to utilize resources more efficiently. Recent reports on sorption-based technologies have shown that post-sorbents with multiple functionalities provide an opportunity for diverse applications. Post-sorption has been explored as a useful method for the manufacture of value-added key products, such as fertilizers, catalysts, nanoparticles, antimicrobial agents, and feed additives. This sustainable materials production pathway is economical and ecologically appropriate. This review summarizes the relevant work on post-sorption applications, strategies, challenges, reported applications, and issues surrounding toxicity. Major challenges involved in the efficient development of these materials for the above applications include the stability of the sorbent, controlling the release rate of an element from the sorbent, and toxicity issues. The major conclusions drawn are as follows:

(i) Adsorption is often used to retrieve various pollutants from aqueous solutions through the use of diverse adsorbent materials, and these could potentially be applied to the production of new value-added products.

(ii) Natural, low-cost materials loaded with macronutrients, such as N and P, can be utilized as fertilizer with controlled slow-release rates in soil applications.

(iii) Prior to the application of post-sorbent as fertilizer or soil conditioner it is essential to determine the levels of PTEs that are present.

(iv) Feed additives, manufactured using various types of biomass, including microbial biomass, can supply the essential trace elements required for animal husbandry.

(v) Carbonaceous metal nanoparticles can be synthesized using biomass laden with metal ions, and successfully used as catalysts and adsorbents.

(vi) Dye-loaded adsorbents could be used to manufacture value-added biochar materials. The dye-loaded sorbent may be further mixed with metal additives to manufacture carbonaceous nanoparticles.

(vii) Regulations should be closely followed when manufacturing feed additives to avoid any subsequent adverse effects.

(viii) Several other applications, such as energy and biological applications (antimicrobial and antioxidant), should be explored more fully.

(ix) Life-cycle analysis (LCA) and the Triple bottom line (TBL) approaches should be carried out to assess the various impacts (environmental, economic, and social) of post-sorption techniques.

Post-sorbent based functional materials will be major players in the development of value-added green materials in the near future. Adsorption technology can be used to engineer custom-tailored post-sorbents that contain a wide variety of functional elements/materials, as outlined.
in this review. More versatile, custom, and facile manufacturing strategies are expected to emerge in the future for the continuous advancement of post-sorbent applications. Though several challenges remain, the rapid development of post-sorbent applications in various fields foreshadows a bright future for sustainable adsorption technology. Since exploration of post-sorbent applications as value-added products has just begun, there is room for further studies in this area to reveal additional opportunities that may exist. Designing and manufacturing green adsorbents using non-toxic and economical precursors will provide an opportunity for successful utilization of post-sorbents loaded with nutrients and elements as feed-additives and fertilizers.

Acknowledgements

This word was financially supported by the Korean Government through NRF (2014R1A2A1A0007378) grants. One of the authors D.H.K. Reddy acknowledges the BK21 plus Postdoctoral Fellowship for financial support.

References


Abbreviations

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<th>Acronym</th>
<th>Description</th>
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<tr>
<td>BC</td>
<td>biochar</td>
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<tr>
<td>CEMNs</td>
<td>carbon encapsulated metal nanoparticles</td>
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<td>CEC</td>
<td>carbon exchange capacity</td>
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<td>CEMNPs</td>
<td>carbon-encapsulated metal nanoparticles</td>
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<td>CEN</td>
<td>European Standardization Committee</td>
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<td>CMC</td>
<td>carboxy methyl cellulose</td>
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<td>CV</td>
<td>Crystal violet</td>
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<td>EDTA</td>
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<td>US Food and Drug Administration</td>
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<td>Fe/FeC@PCS</td>
<td>porous carbon sheets containing carbon-encapsulated Fe/FeC</td>
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<td>International Biochar Initiative</td>
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<td>Mag-PCMA</td>
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<td>MB</td>
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<td>metal nanoparticles</td>
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<td>methyl orange</td>
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<td>MWCNTs</td>
<td>multiwalled carbon nanotubes</td>
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<td>NiO@GNCC</td>
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<td>nanoparticles</td>
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<td>XRD</td>
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