RESEARCH PAPER

Waste Biomass and Biomaterials Adsorbents for Wastewater Treatment

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Abstract

This paper highlights some of the commonly used bio-based materials studied for their applicability as adsorbents in wastewater treatment. Additionally, few processing techniques employed to enhance the ability and or affinity of the adsorbents for wastewater treatment have been discussed. More so, some of the commonly used characterization techniques such as Scanning Electron Microscopy (SEM), Fourier Transform InfraRed (FTIR) spectroscopy among others often employed in a bid to elucidate the properties and morphologies of the adsorbents as well as the potential mechanism(s) underlying the adsorbate-adsorbent interaction(s) has also been extensively conferred. The potential draw-backs, recommendations and future perspectives on the use of bio-based materials as adsorbents in wastewater treatment has also been discussed in the concluding section of this paper.

Keywords: biomass, biomaterials, adsorption, wastewater treatment, adsorbent

1. Introduction

The development of a country is marked/indexed by many indicators including the level of industrialization, development in agriculture as well as urbanization.

Industrialization, municipal activities arising from urbanization, as well as growth in the agricultural activities such as the use of fertilizers, pesticides among others have however contributed directly or indirectly to the ever-increasing concentrations of pollutants such as dyes, heavy metals among other chemicals in

our environment especially our water bodies. The United Nations estimates that three in ten people have shortage/scarcity of clean drinking water [1]. Also, an estimated 3% of ground water is only present in pure form and can be used for drinking and domestic purpose [2, 3]. An ever-increasing trend in the quantities of various contaminants in the hydrological environments implies a continuous reduction and or depletion of the availability of potable water. If not mitigated, nearly half of the world population will be living in areas with scarcity of drinking water [3]. Particularly, the activities of industries such as the textiles, pulp and paper as well as steel produce large quantities of wastewater containing varying concentrations of various contaminants. These when allowed into our environment have the undeniable potential to negatively affect the lives of all living organisms due to the toxic nature of these contaminants. For instance, effluents from the textile industries are usually dye-laden and thus undoubtedly affect the aesthetic appeal of the water even at very low concentrations. The dye contained in these effluents are often toxic and takes a long time to degrade; moreover, these chemicals are carcinogenic or mutagenic for various organisms [4]. Additionally, aquatic habitat is greatly disturbed as a result of the blocking of the sunlight and consequent reduction in oxygen solubility by the presence of the dye molecules. More so, the azo group (–N=N–) found in most synthetic dyes used in this industry is recalcitrant to bio and photo degradation rendering most dyes toxic to life, potential carcinogen and mutagenic. Most heavy metals have the potential to bioaccumulate and are non-biodegradable and thus are harmful to both aquatic life as well as terrestrial inhabitants via the food chain.

Additionally, the presence of organic pollutants which refer to pollutants such as phenols [5], surfactants [6], humic substances [7], monoaromatic compounds [8] etc., released from pesticides, fertilizers, plasticizers oils, detergents, pharmaceuticals are also of great concern, since they are classified as carcinogenic. Commonly all pollutants have associated health implications for living organisms if not treated. As such removing all these pollutants from industrial effluents prior to releasing them into the aquatic environment is expedient and a matter of concern for all stakeholders. Over the years, different techniques have been studied for the purpose of wastewater treatment. These include but not limited to adsorption, ion exchange, biological treatment, precipitation, coagulation, flocculation, reverse osmosis, electrolysis, ozonation, and ultraviolet. However, adsorption which is the accumulation of an adsorbate (pollutant) onto the surface (internal and external) of an adsorbent (solid) is regarded/considered the most suitable technique due to its efficiency, low cost and simplicity and with a reported \$5–200 m^{-3} of water treated using adsorption technique compared to \$10–450 m^{-3} of water treated using other techniques, adsorption is also cost effective. More so, adsorption can be applied to the treatment of most pollutants (organic and inorganic). Many materials including natural materials, biosorbents and waste from agriculture and industry have been

studied for their potential application as adsorbents. This paper highlights the use of biosorbents (waste biomass and biomaterials) as adsorbents. The potential draw-backs, recommendations and future perspective on the use of bio-based materials as adsorbents in wastewater treatment has also been discussed in this paper.

2. *Commonly used biomass and biomaterials*

2.1. Biomass for wastewater treatment

Biomass are basically classified into four main types; agricultural waste, municipal waste, industrial waste, forestry residue, and wood. Due to their abundance, low cost and the presence of several functional groups, biomass has long been studied as adsorbents in wastewater treatment. Especially, agricultural waste can be used as adsorbents for water remediation because of their short regeneration cycle, effectiveness, availability, chemical stability, environmental friendliness, and low cost [9]. Their porous structure and large specific surface area with various functional groups make them easy to adsorb dye and heavy metal ions [3].

Raw agricultural solid wastes and waste materials from forest industries such as sawdust [10], sugarcane bagasse [11], rice husk [12], rice straw [13], maize straw, wheat straw [14] as well as wood shavings [15] have been used as adsorbents. These materials are available in large quantities and may have potential as sorbents due to their physico-chemical characteristics and low-cost. For instance [16], investigated the potential use of peanut hull for the adsorption of six dyes with emphasis on the roles played by major functional groups such as amino, carboxyl, and hydroxyl groups in the overall adsorption potential of the peanut hull. They found that although the presence of carboxyl functional group enhanced the adsorption of cationic dyes, it inhibited the adsorption of anionic dyes whiles hydroxyl group was an important functional group in the adsorption of dyes of both polarities [4]. Also, rice husk has been studied as an adsorbent for the removal of dyes such as Congo red (CR) [17] and heavy metals such as Ni^{2+}, Zn^{2+}, Cd^{2+} and Cr^{6+} [18] as well as organic pollutants such as phenol [19]. Other researchers used rice husk ash as an adsorbent for Hg and Pb [20] removal from aqueous solution. Likewise, adsorption of Cu and Pb ions were successfully adsorbed onto tea waste from aqueous solution [21]. The highest adsorption capacity (48 and 65 mg/g Cu and Pb respectively) was at solution pH range of 5–6 and the overall rate of adsorption was found to be dependent on the adsorbent dose, concentration of the ions in solution, and particle size of the adsorbent. Another study by [22] found tea waste as a prospective adsorbent for the removal of methylene blue (MB) from aqueous solution and had an adsorptive capacity of 85.16 mg/g. Gong *et al.* [23] investigated the potential feasibility of peanut hull for the adsorption of three cationic dyes (MB, brilliant cresyl blue and

neutral red) from aqueous solution. In yet another study by [24], the *Codium decorticatum* alga (green sea weed) was biologically identified and used as a biosorbent for anionic (CR) and cationic dyes [Crystal violet (CV)] from aqueous solutions. Maximum uptake capacities obtained was 278.46 mg/g for CV and 191.01 mg/g for CR. Another common agricultural waste which has been extensively studied for its potential as an adsorbent in wastewater treatment is cashew nut shell. It has been studied for the removal of dyes such as CR dye [25] and metal ions such as Cu^{2+}, Cd^{2+}, Pb^{2+}, and Cr^{2+} from an aqueous solution [26, 27]. In analogous study, cashew nut shell was utilized for the adsorption of Cu ions in solution. The maximum copper adsorption was found to be favored at pH 5.0. and the percentage of Cu ion removed decreased with increasing temperature. Other agricultural solid wastes include orange peels [28], banana peels [29] and wheat straw [30] have all been successfully utilized for the removal of various contaminants from aqueous solution. A recent review reveals that, the maximum Cu adsorption capacities of various bioadsorbents in the order of algae > agricultural and forest > fungal > bacterial > activated carbon > yeast. However, based on the average Cu adsorption capacity, the arrangement can be: activated carbon > algal > bacterial > agriculture and forest-derived > fungal > yeast biomass [29]. Lignocellulose by-products such as sawdust are known to contain several functional groups and have exhibited huge potential as an adsorbent. Particularly, a study by Long *et al.* [31], indicated the presence of hydroxyl and carboxyl functional groups. Hence, the NaOH treated *Michelia figo* wood sawdust was effective for the removal Pb^{2+}, via binding to the hydroxyl and carboxyl functional groups. Interestingly, the authors reported that, although in a mixed system, the presence of Cd^{2+} and Cu^{2+} had no significant effect on the adsorptive capacity of the sawdust for Pb^{2+}, the presence of Pb^{2+} significantly reduced the removal of Cd^{2+} and Cu^{2+}.

2.2. Common characterization techniques and functional groups found in waste biomass used as adsorbents

The characterization of adsorbents is done in the quest to elucidate important information about the structure and properties of the adsorbents and possibly the interaction between the adsorbents and adsorbates. Researchers utilize characterization tools such as Fourier transform infrared (FTIR) spectroscopy, scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX), Brunauer–Emmett–Teller analyzer (BET), and elemental analysis (EA).

Fourier transform infrared (FT-IR) spectroscopy is a technique that employs a high-intensity IR beam which, when made incident on or passed through a test sample, is partly absorbed by the sample, yielding an absorption spectrum. This is because each type of bond in a molecule, upon absorbing IR energy, vibrates at a specific resonant frequency depending on the bond geometry and atomic masses

involved. The FT-IR spectrum is usually reported as a plot of transmittance (%) or absorbance versus wavenumber (cm^{-1}) [32]. For instance, in a study by [29], FTIR spectroscopy was used to show the functional groups present on the surface of banana and orange peels, two very common agricultural waste. As is characteristic of most agricultural waste, many functional were found on the surfaces of the peels. Specifically, the broad peaks found at 3421.6 cm^{-1} and 3422.43 cm^{-1} were attributed to a possible involvement of hydroxyl groups while the peaks at 2923.06 cm^{-1} and 2924.75 cm^{-1} was due to CH stretching vibrations of CH, CH$_2$, and CH$_3$ groups. The absorption bands at around 1637.45–1637.65 cm^{-1} to 1384.45–1438.70 cm^{-1} were characteristics of C=C in aromatics rings. C–O carboxyl band was associated with the peaks observed at 1383.45 cm^{-1} and 1236.34 cm^{-1}. Furthermore, peaks at 1054.40 cm^{-1} and 1071.46 cm^{-1} were attributed to Si–O stretching and Si–O. In yet another interesting study by [33], the absorption peaks at 1639 cm^{-1}, 1068 cm^{-1}, 929 cm^{-1} and 849 cm^{-1} obtained from the FTIR analysis of k-carrageenan adsorbent were assigned to bending vibration of O–H (in water molecules), stretching vibration of C–O (in the glycosidic linkage of 3,6-anhydro-D-galactose), stretching vibration of C–O (in polyhydroxy groups), stretching vibration of C–O–SO$_3$ (in D-galactose-4-sulfate), respectively. Details of the surface morphology of an adsorbent is obtained using the Scanning Electron Microscopy (SEM) while the energy dispersive X-ray (EDX) spectroscopy provides information on the elemental constituents of the adsorbent. The elemental analyzer is utilized when quantitative information of the elemental constituents mainly CHNS (O) of the adsorbent is desired. Quantitative measure of the other elemental constituents can be obtained from X-ray photoelectron spectroscopy (XPS) or inductively coupled plasma optical emission (ICP-OES) also known as inductively coupled plasma atomic emission (ICP-AES) or the Inductively coupled plasma atomic absorption (ICP-AAS) spectroscopic analyses. Additionally, X-ray diffractometry (XRD) is used when there is the need to identify the phase of a crystalline material. Thus, although the XRD may not be a very useful analytical tool for purely biomaterials, it is a very important tool especially in analyzing bio-metal oxide composite materials with potential to be used as an adsorbent such as chitosan-hematite adsorbent.

2.3. Modified agricultural-waste as adsorbents for wastewater treatment

Although, the use of these agricultural-waste (plant-based) adsorbents in pristine or raw form helps to decrease the cost of disposal of these wastes and provide an alternative to help solve the ever-rising environmental menace, research points to the fact that in most cases, there is the need to modify the material in order to increase the adsorption efficiency, stability, recyclability so that it can be used practically [3]. A comparison between the raw and treated adsorbents has been extensively discussed in a recent review by [3]. From the literature reviewed, it was

clearly demonstrated that chemically treated agricultural waste showed comparatively significant removal efficiency than the raw agricultural waste [3, 4].

2.3.1. Physical modification of agricultural waste used as adsorbents

Plant-based-agricultural waste adsorbents can be modified by using different physical processes such as grinding, cutting, drying, milling, boiling, thermal drying, carbonization among others. These treatment methods generally change the particle size distribution, surface area and moisture content of the adsorbent. Utilization of physically modified plant-based agricultural waste adsorbents for heavy metal ions and dye removal are discussed in a review by Yadav *et al.* [3]. Cucumis sativus peel was considered a nano biosorbent after it was modified by grinding such that the particles of spherical shape with variable sizes from 23 to 78 nm were obtained. The nano-biosorbent was successfully utilized for the removal of CV from wastewater with an adsorptive capacity of 149.25 mg/g [34]. Also, a study by [35] showed that milling of sugarcane bagasse resulted in an increase in the surface area from 0.58 to 0.66 m^2/g^{-1} which resulted in 5.6% rise in (MB) dye removal efficiency. Moringa oleifera pod husk also showed a spontaneous and exothermic adsorption of CV dye (156.25 mg/g) because of increase in the surface area and average diameter of pore after grinding [36]. Grinding modification of fava bean peels resulted in production of macro porous adsorbent which had surface area and pore volume of 0.2108 ± 0.0035 m^2/g and 0.00067 cm^3/g respectively. The grounded fava bean peels were successfully used for the biosorption of MB dye from aqueous solutions with a reported maximum capacity of 140 mg/g [37].

2.3.2. Thermochemical treatment of biomaterials

In the quest to find a lasting solution to curb the pollution of water bodies, research have studied and applied varying technique with the aim of producing a material/adsorbent with enhanced properties. One such technique is the thermal treatment of low-cost biomass under little-to-no oxygen condition which leads to the production of a black porous carbonaceous materials known as biochar [38–40] as well as condensable and non-condensable gases (pyrolysis). Other thermal processes including hydrothermal carbonization and gasification have been extensively discussed and compared in a recent review by [41].

Biochar is typically produced from materials that are naturally abundant such as agricultural residue, animal waste, algae, sewage sludge, manures, and organic municipal solid wastes or refuse of woody plants that have high carbon content [38, 41]. Biochar have found use in various facets of environmental remediation including soil remediation [42], environmental pollution among others. Particularly in environmental pollution control, biochar is proved to be an effective, low-cost, and environment-friendly adsorbent capable of handling varying contaminants such as dyes, metals, emerging pollutants. Many researchers attribute this to its relatively

large surface area and abundant surface functional groups [43, 44]. Biochar can be used for adsorbing metals/metalloids and purifying water [45]. For instance [46], reported the effective removal of Pb^{2+} from aqueous solution using biochar produced fresh (193 mg/g) and dehydrated (359 mg/g) banana peels. As expected, the FTIR analysis revealed the presence of abundant surface functional groups such as hydroxyl and carboxyl which greatly enhanced the adsorption performance with the change of the C=O/O–C=O and to of Pb–O/Pb–O–C on the surface of the adsorbent after adsorption suggesting that the ion exchange might be the dominant mechanism. Notwithstanding, the effectiveness of biochar as an adsorbent is related to the factors such as the biomass type, biomass pretreatment, pyrolysis temperature and post pyrolysis treatment as well as heating rate and residence time. This is because, research suggests they can affect the compositions and physicochemical properties of the biochar and hence the adsorptive performance of the biochar produced. For example [47], found that the effectiveness of removing Cd and Ni from wastewater was greatly influenced by the type of the biomass compared to the pyrolysis temperature. Particularly, when rated on the bases of the percentage removal and removal capacity for Cd and Ni from aqueous solution the biochar adsorbents had the following ranking: Chicken manure mixed with sawdust > sugarcane straw > rice husk > sawdust. It is well known that increasing pyrolysis temperature tends to reduce the yield of biochar while the ash and or inorganic content increases. Also, a study by [40], different biochar produced from rice straw (RS), wood chip (WC), and Korean cabbage (KC) studied for their applicability in wastewater treatment using CR and CV as model dyes. They found that, initial solution pH had little effect on CR and CV adsorption onto all biochars and that, the ash content and surface functional groups were controlled the overall adsorption process. More so, they reported that, all biochars studied were more effective for the removal of CV [KC (1304 mg/g) > RS (620.3 mg/g) > WC (195.6 mg/g)] compared to CR [RS (190.8 mg/g) > WC (110.0 mg/g) > KC (95.81 mg/g)]. In yet another study, the effects of water washing pretreatment process on the property and adsorption capacity of Saccharina japonica macroalgae-derived biochars was investigated [48]. The study showed that, by washing pretreatment, the specific surface area of the biochars can dramatically increase. albeit with only a slight increase in the porosity. Particularly, biochars were carbonaceous microporous materials (67–80% micropore volume), with specific surface areas between 543–188 m²/g. Again, the washed biochars exhibited a significantly lower ash content (26–35%) than unwashed biochars. When used as an adsorbent, the washed biochar was effective in removing CV from aqueous solution with a maximum adsorptive capacity of (1277 mg/g).

2.3.3. Chemical modification of agricultural waste used as adsorbents

Chemical modification is a direct surface treatment method that alters the structure and surface properties of precursors due to the interaction between a modifying

agent and a precursor [49]. The chemical modification process eliminates or incorporates new functional groups or elements onto the surface of the precursor thus increasing the number of active binding sites and also increasing the ion-exchange properties of the material with the adsorbates [50]. Different chemical treatment methods are employed to achieve different surface properties for different agricultural wastes. These treatment methods include acid treatment, alkaline treatment, grafting, solvent extraction and salt impregnation [51]. For instance, Feng *et al.* [52] used methyl acrylate in the grafting of orange peels cross-linked with epichlorohydrin. They reported a 4.2, 4.6- and 16.5-folds increase in adsorption of Pb^{2+}, Cd^{2+} and Ni^{2+} respectively by the modified orange peels compared to the raw orange peels. The modified orange peels could remove up to 476.1, 293.3 and 162.6 mg of the Pb^{2+}, Cd^{2+} and Ni^{2+} ions respectively for every gram of the adsorbent. Also [53], treated cashew nut shells with sulfuric acid for the removal of Cu^{2+}, Cd^{2+}, Zn^{2+} and Ni^{2+} ions. The studies indicated a maximum adsorption of 406.6, 436.7, 455.7, 456.3 mg/g for the respective ions. In yet another study [54], modified sugarcane bagasse in three ways: treatment with sodium hydroxide, treatment with citric acid, and treatment with sodium hydroxide followed by treatment with citric acid. The prepared adsorbents were used for the removal of Cu^{2+} ions. The researchers found that the sugarcane bagasse treated with only citric acid was the most effective for Cu^{2+} ions uptake with a maximum adsorption capacity of 31.53 mg/g. Additionally [55], used nitric acid as a modification agent for the oxidation of corn stalk for the removal of Cu^{2+} ions. They also found that the modified corn stalk with a maximum adsorption capacity of 20.65 mg/g showed a higher affinity for Cu^{2+} ions than unmodified corncob and unmodified corn stalk even though these two also exhibited a relatively high adsorption of the copper ions. A list of some common chemically modified biobased materials used as adsorbents has been presented in table 1.

2.3.4. *Activated carbon using biomaterial precursors for wastewater treatment*

Activated carbon is an amorphous carbonaceous material with high porosity. It has a large internal surface and a good pore structure and surface chemistry making it an excellent adsorbent for air pollution control [56], food processing, purification of drinking water and wastewater treatment [57], metal recovery [58] as well as catalysis [59]. It is the most common adsorbent used for a vast array of pollutants such as organic and inorganic pollutants, polar and non-polar compounds from aqueous and gaseous environments. Due to its wide range of applications, the demand for activated carbon is high and is projected to rise in the future as countries seek to meet environment compliance regulations.

Activated carbon is produced from organic compounds rich in carbon with little or no tendency to fuse upon carbonization. The selection of these biomaterials as precursors is usually based on a given criterion; likelihood of producing a good

Table 1. Chemically modified agricultural waste biomass adsorbents.

Precursor	Modifying agent	Adsorbate	Adsorptive capacity (mg/g)	Ref.
Cashew nut shells	Sulfuric acid	Cu^{2+}	406.6	[53]
		Cd^{2+}	436.7	
		Zn^{2+}	455.7	
		Ni^{2+}	456.3	
Orange peels	Methyl acrylate	Pb^{2+}	476.1	[52]
		Cd^{2+}	293.3	
		Ni^{2+}	162.6	
Sugarcane bagasse	Citric acid	Cu^{2+}	31.53	[54]
Wheat straw	Sodium hydroxide	Cd^{2+}	3.08	[64]
		Cr^{2+}	7.55	
		Pb^{2+}	21.24	
Corncob	Sodium hydroxide	Cd^{2+}	19.86	[65]
		Cr^{2+}	34.97	
		Pb^{2+}	56.67	
Banana peels	Acrylonitrile	Cr^{6+}	6.17	[66]
Banana peels	Acrylonitrile	Mn^{2+}	5.73	[67]
Banana stalk	Sodium hydroxide	Cd^{2+}	5.82	[65]
		Cr^{2+}	13.35	
		Pb^{2+}	59.39	
Okra biomass	Succinic anhydride	Cu^{2+}	72.72	[68]
		Zn^{2+}	57.11	
		Cd^{2+}	121.51	
		Pb^{2+}	273.97	
Chickpea husks	Potassium hydroxide	Pb^{2+}	135.8	[69]
		Cr^{6+}	59.6	
		Cu^{2+}	56.2	
Sunflower achene	Sodium hydroxide	Cd^{2+}	14.28	[65]
		Cr^{2+}	20.36	
		Pb^{2+}	39.23	

activated carbon, cost and availability, low inorganic matter, low degradation upon storage and ease of activation. The traditional raw materials used in the production of activated carbon include coal [60], coconut shell [61], wood [62], peat [59], nut shells [63] etc., sometimes also synthetic high polymers. Thus, most lignocellulosic materials with high carbon content can potentially be activated. However, activated carbon derived from agricultural biomass has some benefits of low cost and

efficiency compared with non-renewable coal-based activated carbon. Agricultural biomass serves as a rich source of raw material for activated carbon production due to it shear abundance and availability.

In recent years, there has been an increased interest in finding cheaper alternative source of raw material for activated carbon production. A lot of studies have been conducted on activated carbon from agricultural biomass. Liu *et al.* [70] investigated the production of activated carbon from bamboo by microwave-induced phosphoric acid activation. The results show a large acidic surface area with mainly microporous structure. Sych *et al.* [71] also studied the production of activated carbon from corncob using phosphoric acid as the chemical activator. This resulted in a highly porous activated carbon containing large amount of acid surface groups. Afdhol *et al.* [72] investigated the production of activated carbon from palm shells using KOH and $ZnCl_2$. In another study [73], observed that production of activated carbon from rice husk yielded a highly porous activated carbon with large surface area. Similar studies have been conducted on other agricultural biomass such as jute fiber, apple waste [74], cherry stone, walnut shell, banana peel [75], cotton stalk and sugarcane bagasse.

2.4. Other biomaterials commonly used for wastewater treatment

A survey of literature reveals natural/bio-polymers and their derivatives have also been studied for their potential to adsorb various classes of pollutants from wastewater. The increasing number of publications on adsorption of toxic compounds by modified polysaccharides shows that there is a recent increase in interest in the synthesis of new low-cost adsorbents used in wastewater treatment [76]. Materials such as chitosan, alginate and carrageen are at the forefront of this upsurge and have duly received considerable attention as potential adsorbents in wastewater treatment.

2.4.1. Chitosan

Chitosan (CS) or (β-(1 →4)-N-acetyl-d-glucosamine), is a biocompatible, biodegradable, and nontoxic polysaccharide obtained from the deacetylation of chitin, the major component of the exoskeleton of crustaceans such as shrimps, nephrops (lobsters) as well as from terrestrial organisms such as silkworms, honeybees, and mushrooms [77]. Research has shown that CS has higher affinity for contaminants such as dyes particularly, anionic dyes [78] and heavy metals ions [79] in industrial effluents due to the abundance of amine and hydroxyl groups functional groups which is related to the degree of acetylation as reported by [80]. For instance, in [81, 82], the interaction between CS and anionic dyes was investigated. The investigations clearly indicated that CS had a natural selectivity for anionic dye molecules and was very useful for the treatment of wastewater.

Comparatively, recent studies have indicated that, CS adsorbent showed a higher adsorptive capacity of dye molecules than commercial activated carbon (CAC) and other low-cost adsorbents [76]. Although various forms of CS exist, initial studies of application of CS in wastewater treatment was dominated by the flaked or powdered form [78]. However, recent studies suggest that, CS hydrogels and beads are currently preferred to the flakes or powder forms of the polymer due to the low surface area, high crystallinity, poor acid and mechanical properties, lack of porosity and more importantly, low adsorptive capacity of the latter [82, 83]. Thus, chitosan-based hydrogels have a special place in the field of industrial wastewater treatment because of their fast kinetic, high adsorption capacity, and favorable reusability [84].

2.4.1.1. Chitosan-based adsorbents   One other unique property of CS is its ability to dissolve in weak acids such as acetic acid and formic acid leading to the protonation of the $-NH_2$. Hence, CS becomes a cationic polyelectrolyte and can thus interact with negatively charged ions or polyelectrolytes leading to the formation of a 3-D hydrogel structure (Hydrogels are three-dimensional, flexible and porous networks that swell in water and biological fluids due to the presence of hydrophilic groups like hydroxyl, carboxyl, and amide [84]). In view of this, many researchers have explored the applicability of the CS hydrogels in wastewater treatment. For instance, Chatterjee *et al.* [85] reported a relatively new CS hydrogel (HC) adsorbent formed via anionic surfactant gelation. The HC had a core-shell structure and exhibited enhanced mechanical and acid stability. Additionally, the HC was effective for the adsorption of both anionic and cationic dyes [85, 86]. Also, CS hydrogel adsorbent formed via alkali (NaOH) gelation has been utilized for the removal of dyes from aqueous solution.

2.4.1.1.1. *Chitosan-based hydrogels for wastewater treatment*   Another prominent reason for which CS-based hydrogels have gained immense interest among researchers is the propensity to incorporate other ingredients such as nano-materials, bacteria, powdered biochar, activated carbon powder among ours into the hydrogel matrix mostly in-situ the gelation process. This has led the inception of composite CS-hydrogels. Incorporation of inorganic materials into hydrogels is a promising approach to increasing adsorptive capacity as well as other important properties such as selectivity, thermal, chemical and mechanical stability of the hydrogels.

In line with this [87], prepare chitosan-halloysite nanocomposite hydrogel beads by phase inversion method for removal of MB and malachite green (MG) dyes. The thermal gravimetry analysis (TGA) of the resulting composite hydrogel indicated that, the presence of the halloysite nanotubes within the hydrogel beads enhanced the thermal stability. Also, the presence of the halloysite nanoparticles increased the roughness of both the internal and external surfaces there by improving the

adsorptive capacity of the hydrogel for the two dyes. Adsorption of MB is faster than MG and equilibrium adsorption reaches within 40 min for MB and about 7 days for MG. Moreso, chitosan/ZnO nanocomposite hydrogel prepared using sodium triphosphate penta-basic for removal of RB5 has also been studied [88]. Likewise, the thermal stability of the as-obtained hydrogel was enhanced and the positive value of ΔH° and negative value of ΔG° indicated an endothermic and spontaneous nature of the adsorption process, respectively. Zhu *et al.* [89] synthesized macroporous CS–g–P(AA) hydrogel stabilized by modified Fe_3O_4 nanoparticles via pickering high internal emulsions template method for removal of Cd^{2+} and Pb^{2+} from wastewater due to adjustable porous structures and the existence of many functional groups like carboxyl, hydroxyl, and amino.

For instance, CS-based nanocomposite hydrogels produced via anionic surfactant gelation has been reported. In particular, when the hydrogels were incorporated with goethite nanoparticles, a multi-membrane hydrogel structure (MHC) was produced whiles when hematite nanoparticles were incorporated, an extensively porous hydrogel material was obtained. Both hydrogels were highly effective in adsorbing CR from aqueous solution with the latter having one of the highest adsorptive capacities (4705.6 mg/g) ever reported in literature which was about 26.7 times that of the pristine CS hydrogel adsorbent (176.5 mg/g) [90, 91]. Some chitosan-based adsorbents are presented in table 2.

Currently, most researchers investigate the potential of CS-based hydrogels for the removal of emerging pollutants. The prominent classes of emerging pollutants are pharmaceuticals, pesticides, wood preservation, and industrial chemicals [84]. Depending on the chemical structure of the pollutants, chitosan-based hydrogels adsorb them from aqueous solutions through complexation, electrostatic interaction, and hydrogen bonding [84]. Particularly, for aromatic hydrocarbons, the results show that the hydrogels have good adsorption capacity for a variety of aromatic hydrocarbons through $\pi-\pi$ interactions, which decreases after the adsorption-desorption cycle [101]. For example, the removal of ciprofloxacin from aqueous solutions was investigated using chitosan/biochar hydrogel beads (CBHB). The results showed that the adsorption rate was almost independent of the temperature. However, the adsorptive capacity decreased from 34.90 mg/g to 15.77 mg/g in the presence of 0.01 N Na_3PO_4 whereas other electrolytes such as NaCl, Na_2SO_4, $NaNO_3$ with same concentration did not affect the sorption capacity. Notwithstanding, increasing concentration of NaCl resulted in a slight decrease in the adsorption capacity of the chitosan/biochar hydrogel beads. The removal of ciprofloxacin was attributed to a mixed mechanism of $\pi-\pi$ electron donor-acceptor interaction, hydrogen bonding and hydrophobic interaction [102]. Again, powdered leached carbon black waste (LCBW)-CS composite beads prepared via instantaneous gelation method was successfully utilized as an adsorbent for the

Table 2. Chitosan-based adsorbents for wastewater treatment.

Adsorbent	Adsorbate	Adsorptive capacity (mg/g)	Reference
Chitosan-based magnetic composite $(CTS@SnO_2@Fe_3O_4)$ CTS@Fe_3O_4	Reactive Brilliant red	1080.34 749.76	[92]
Fe-load chitosan	Methyl orange	205	[93]
Poly(vinyl alcohol)/chitosan composite	Malachite green	380.65	[94]
	Cu^{2+}	193.39	
Hematite@chitosan core/organically shell nanocomposite	Pb^{2+} Cu^{2+} Cd^{2+}	129.8 63.2 69.9	[95]
Magnetic/chitosan/graphene oxide(MCGO) 3D nanostructure	Dispersive blue 367	298.27	[96]
Triethylenetetramine-chitosan/alginate composite beads	Cr^{6+}	241.38	[97]
Chitosan-alginate nanoparticles	Hg^{2+}	217.39	[98]
Chitosan(CHT)/Alginate(ALG) $CHT/ALG/Fe_3O_4@SiO_2(1)$ $CHT/ALG/Fe_3O_4@SiO_2(8)$	Pb^{2+}	217.24 220.68 245.28	[99]
Magnetic chitosan/graphene oxide (MCGO) composite	Pb^{2+}	112.35	[100]

removal of tetracycline (TC) and amoxicillin in distilled and tap water. It was observed that the effect of cations present in the tap water was insignificant to adsorption performance of the LCBW-CS composite bead although it enhanced that of the LCBW. When used as adsorbent in a fixed bed column, the experimental data obtained fitted well to the Adams-Bohart model and Thomas model.

Chitosan-based adsorbent have huge prospects due to properties such as high adsorption capacity and adsorption efficiency, organization and structure favorable for adsorption, desirable reusability, low cost, as well as good biodegradability and environmental friendliness [101]. Extensive discussion on removal of different dyes from aqueous solutions by bio-based adsorbents have been outlined in a study by Wang and Zhuang [103].

2.4.2. Alginate

Alginates are linear unbranched polymers containing β-(1, 4)-linked D mannuronic acid (M) and β-(1, 4)-linked L-guluronic acid (G) residues, which are negatively charged polymers obtained mostly from brown seaweed walls. Monovalent ions such as sodium and ammonium interact with the carboxyl groups of alginic acid to form water-soluble salts although alginic acid is essentially insoluble in water [77]. Sodium alginate, which is a sodium salt of alginic acid contained in alginates, is considered a good candidate as an adsorbent for wastewater treatment due to its non-toxicity, high water permeability, stability and biodegradability. The presence of carboxyl and hydroxyl functional groups on the alginate polymer chain enhance significant interactions between alginate and several types of adsorbates such as heavy metals and dyes making alginate a suitable material to be used as an adsorbent [104, 105].

2.4.2.1. Alginate-based hydrogels for wastewater treatment   Alginate salt solubilizes in water to form a viscous aqueous solution with a negative charge on the polymer due to the presence of abundant carboxylic acid functional groups. As such, when droplets of the solubilized alginate solution contacts divalent cations such as Ba^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+}, gelation occurs almost instantaneously. However, complete gelation occurring after progressive diffusion of the divalent ions into the core of the droplet [106]. 3D structures called hydrogels is thus formed. Other researchers have utilized crosslinkers including glutaraldehyde, epichlorohydrin, concentrated sulfuric acid, and formaldehyde [105] to produce alginate-based hydrogels with capability of being used as low-cost adsorbents in wastewater treatment. For example [107], prepared calcium alginate hydrogel beads and studied its performance in the treatment of aqueous solutions containing methyl violet. The authors reported that the prepared adsorbents could remove methyl violet up to 889 mg/g. Besides, Lu *et al.* [108] synthesized sodium alginate hydrogel by liquid-liquid phase separation technique and post-crosslinking reaction. Upon examining the prepared adsorbent in the removal of selected dyes and heavy metals, results showed maximum adsorption capacities of 572, 54.9, 82.8, 135.5 mg/g for methylene blue, Cu^{2+}, Ag^+, and Fe^{3+} ions respectively. Pure alginate hydrogels however have limited use due to their dense structure, relatively low stability and mechanical strength [104]. As such, current studies on alginate hydrogels as adsorbent focus on the development of alginate composite hydrogel adsorbent via the incorporation of different active compounds ranging from engineered nanoparticles, carbonaceous materials and powders, and other polymers with good stability, large specific surface areas, good mechanical strength, and abundant surface functional groups have been combined with alginate hydrogels to achieve synergetic benefits [105]. In a study by [109], carboxylated cellulose nanocrystals were incorporated into calcium alginate hydrogel beads for the removal of Pb^{2+} ions

from aqueous solutions. The adsorbent had excellent affinity for the Pb^{2+} ions with a maximum uptake capacity of 338.98 mg/g. After five repeated cycles, the maximum adsorption capacity was satisfactorily maintained at 223.2 mg/g. Mohammed *et al.* [110] also prepared cellulose nanocrystal/alginate hydrogel beads and used it in the adsorption of MB in aqueous solutions. Again, the removal efficiency after five repeated cycles was well maintained at 97% of the initial maximum adsorption capacity of 256.41 mg/g. In the context of alginate-carbonaceous composites, Yang *et al.* [111] synthesized sodium alginate/graphene oxide double network hydrogel beads for the removal of Mn^{2+} ions; a maximum adsorption capacity of 56.49 mg/g was reported by the authors. In yet another study [112], synthesized porous carbon/Fe_3O_4/alginate hydrogel beads which demonstrated excellent affinity for MB with a maximum adsorption capacity of 49.66 mg/g. Some alginate-based adsorbents used in wastewater treatment are presented in table 3.

3. Future perspective

There is an undeniable fact that massive strides have and are been made in the area of wastewater treatment by all stakeholders especially researchers especially in area of material development for use as an adsorbent. However, there is still a long way to go and higher heights to be attained in this noble area of research. Particularly, although wastewater from major contributing industries such as textiles, pulp and paper, leather among others is a complex cocktail of diverse contaminants ranging from heavy metals to dyes, organic debris, not forgetting the presence of some common salts, most of the results reported by researchers using bio-based adsorbents are based on laboratory-prepared samples which are usually void of the complex constituents associated with real wastewater samples. Research suggests that, the results obtained in the laboratory can significantly deviate from the that obtained during real-time (practical) application and or using real wastewater sample [123]. As such, future research should therefore pay attention to this issue so as to facilitate the practical use of bio-based adsorbents in wastewater treatment. Again, it is well established that reducing the particle size results in an increase in surface area of adsorbents. However, the use of powdered bio-based adsorbents like activated carbon, biochar among others has associated engineering issues such as pressure drop, hydrodynamic conductivity in column studies and applications as well as high post treatment energy required in separating the loaded adsorbent and the treated wastewater [124]. As such, incorporation of bio-based powdered adsorbents into platforms leading to the production of stable composite adsorbents will enhance its prospects for large-scale application.

Table 3. Alginate-based hydrogels used for wastewater treatment.

Adsorbent	Adsorbate	Adsorptive capacity (mg/g)	References
Carboxylated cellulose nanocrystal/sodium alginate hydrogel beads	Pb^{2+}	338.98	[109]
Alginate-kelp biochar composite hydrogel bead	Crystal violet	4545.70	[113]
Sodium alginate crosslinked acrylic acid/graphite hydrogel	Malachite green	628.93	[114]
Titania incorporated sodium alginate crosslinked polyacrylic acid hydrogel nanocomposite	Methylene blue	2257.36	[115]
Sodium alginate/polyethyleneimine hydrogel	Cu^{2+} Pb^{2+}	322.60 344.80	[116]
Acrylic acid-grafted sodium alginate-based TiO_2 hydrogel	Methyl violet	1156.60	[117]
PVA-alginate encapsulated Prussian blue graphene oxide hydrogel beads	Cs	164.50	[118]
Porous graphene/alginate double network nanocomposite beads	Methylene blue	2300	[119]
Amino-carbamate moiety grafted calcium alginate hydrogel beads	Ag^+	210	[120]
Amidoxime modified polymers of intrinsic microporosity/alginate hydrogel beads	Malachite green	1023	[121]
Lanthanum-sodium alginate hydrogel	Direct green Acid blue	909 983	[122]

4. Conclusion

The wide range of biosorbents presented here have indicated outstanding capacities in the removal of various pollutants from the aqueous environment. The potency of these materials as adsorbents is based mainly on their structure and the presence of abundant surface functional groups which can even be further enhanced by physical, chemical and thermochemical treatments. Additionally, the possibility of combining these materials with other materials presents an even greater avenue to produce adsorbents with significantly improved properties which can be utilized for the removal of different classes of pollutants as compared to the pristine biomaterials. Overall, the unique characteristics of these materials including their biodegradability, nontoxicity, availability, and relatively lower cost demonstrate their huge potential to be employed as efficient, economic and environmentally friendly materials in industrial wastewater treatment and thereby pollution control.

Data availability

Data sharing is not applicable to this article as no new data were created in this study.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work.

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