Chapter

Heavy Metal Removal by Alginate Based Agriculture and Industrial Waste Nanocomposites

Shivangi Omer

Abstract

The use of biopolymers and nonliving organisms as sorbents is one of the most promising techniques because they contain several functional groups which show different affinities towards various metal ions. Alginate is naturally occurring anionic biopolymer extracted from brown algae. It also contains numerous applications in biomedical science and engineering due to its favorable properties and ease of gelatin. This chapter represents a overview based on alginate based agriculture and industrial waste nanocomposites and found that limited studies are reported for combination of alginate with industrial/agriculture waste in nanoscalic material so far, but this review study enlightening the several studies based on nanocomposite combinations of alginates and biopolymers and these biopolymers can also be derived from various agro/industrial waste by simple chemical and mechanical methods. So, we should work on the formulation of alginates agro/industrial waste nanocomposites. Preparation of alginate nanomaterials with agriculture/industrial waste constituents confirms its effectiveness in water purification. In the environment, we can control its reutilization by desorption studies. Another advantage is that it can be transform from nanoparticles to nano polymeric films and support to batch adsorption process to fixed bed column in form of large-scale application.

Keywords: Alginate, agriculture waste, industrial waste, nanocomposite, adsorption, heavy metals

1. Introduction

Alginate is naturally occurring anionic polymer typically obtained from brown seaweed and commercially available alginate extracted from brown algae (Phaeophyceae), including *Laminaria hyperborea*, *Laminaria digitata*, Laminaria japonica, *Ascophyllum nodosum*, and *Macrocystis pyrifera*. Alginate is calcium, magnesium, and sodium salt of alginic acid which is a linear structure of heteropolysaccharide and composed of d-mannuronic acid and l-guluronic acid.

It is biodegradable, biocompatible, renewable, nontoxic and moderately efficient because of their low molecular weight, high shear stability and easily available from reproducible farm and forest resources. It also contains numerous applications in biomedical science and engineering due to its favorable properties and ease of gelatin [1]. As its utilization in agriculture application, it functions as soil conditioner. Alginate is natural materials that can absorb large amount of water, as much as hundreds of times of their own mass and can form ionic and nonionic moisture-holding hydrogels which increase soil water retention capability. So, alginate is excellent superabsorbent or water retaining material and can serve as a good carrier to uptake metal ions from aqueous solution [2].

The use of biopolymers and nonliving organisms as sorbents is one of the most promising techniques because they contain several functional groups which show different affinities towards various metal ions. As we say earlier, alginate is component of outer cell of brown algae but commercially it exist as sodium alginate (SA) which shows viscous nature after dissolving in water, but when it is utilized for removal of metal ions, it is usually prepared as Calcium Alginate. Biopolymers contains many potential binding sites such as carboxylate, amine, phosphate, sulfate, hydroxyl and other chemical functional groups. And due to availability of these free binding sites enhance surface charges. As a result, increase uptake of metals ions. Binding with these free active sites largely depend on pH of the aqueous solution and various metal ions shows different adsorption capacity at different pH scale. As a point of view of alginates chemical structure, Sodium alginate (SA) is rich in hydroxyl (OH) and carboxyl (COOH) functional groups and extra negatively charged sites, which are the foremost groups involved in heavy metal adsorption. Alfaro-Cuevas-Villanueva et al. evaluated the removal of lead and cadmium using calcium alginate beads as biosorbents under the influence of various pH range and temperature [3].

But a potential problem with alginates derivatives are their poor strength and flexibility towards high hydrophilicity. Which can be overcome by chemical modification with various biobased polymers such as cellulose, starch, chitosan, xylene, lignin. It will not only modify properties related with basic structure but also will enhance biocompatibility and biodegradability of compound. Of course, hydrophilicity of these hybridized copolymers introduces water fluxes with greater adsorption capacity higher than most of the synthetic polymers which also a green approach to environment.

In terms of operational costs and ease to use, adsorption is the most promising techniques among all the techniques reported in various literature. Adsorption allowing the treatment waters gives rise to a very rich bibliography through a very great variability of adsorbents.

Since this chapter include contents about alginate-based agriculture/industrial waste nanocomposites, there is a need to brief about agriculture/industrial waste.

2. Agriculture waste/industrial waste

2.1 Agriculture waste

Various wastes related agriculture cropping, processing or harvesting are called as 'Agriculture waste'. Agriculture waste are bioactive compounds which are rich in nutrients such as cellulose, lignin, xylene and fibers. Agriculture based industries produces huge number of residues as waste product every year which are dumped to the open ground area and release to environment without proper disposal. But these residues can be used utilized as alternate source in various application such as biogas, biofuels, as an adsorbent for heavy metal, in mushroom cultivation and as raw material in various industries that can help to reduce the production cost and relived the pollution load of environment. Various organizations defined agro-industrial waste by different ways.

Obi et al. reported, Agricultural wastes are defined as the residues from the growing and processing of raw agricultural products such as fruits, vegetables, meat, poultry, dairy products, and crops [4]. They are the unwanted outputs of production and processing of agricultural products that may contain material that can benefit man but whose economic values are less than the cost of collection, transportation, and processing for beneficial use [5–7].

Their composition of agriculture waste will depend on the system and type of agricultural activities takes place after the process of cropping and they can be in various forms such as liquids, slurries, or solids. Agricultural waste are also called as agro-waste is which comprised of natural, animal waste (manure, animal carcasses), food processing waste (only 20% of maize is canned and 80% is waste), crop waste (corn stalks, sugarcane bagasse, drops and culls from fruits and vegetables, prunings) and hazardous and toxic agricultural waste (pesticides, insecticides and herbicides) etc. [4, 5]. **Figure 1** illustrates a simple classification of agriculture waste based on its source.

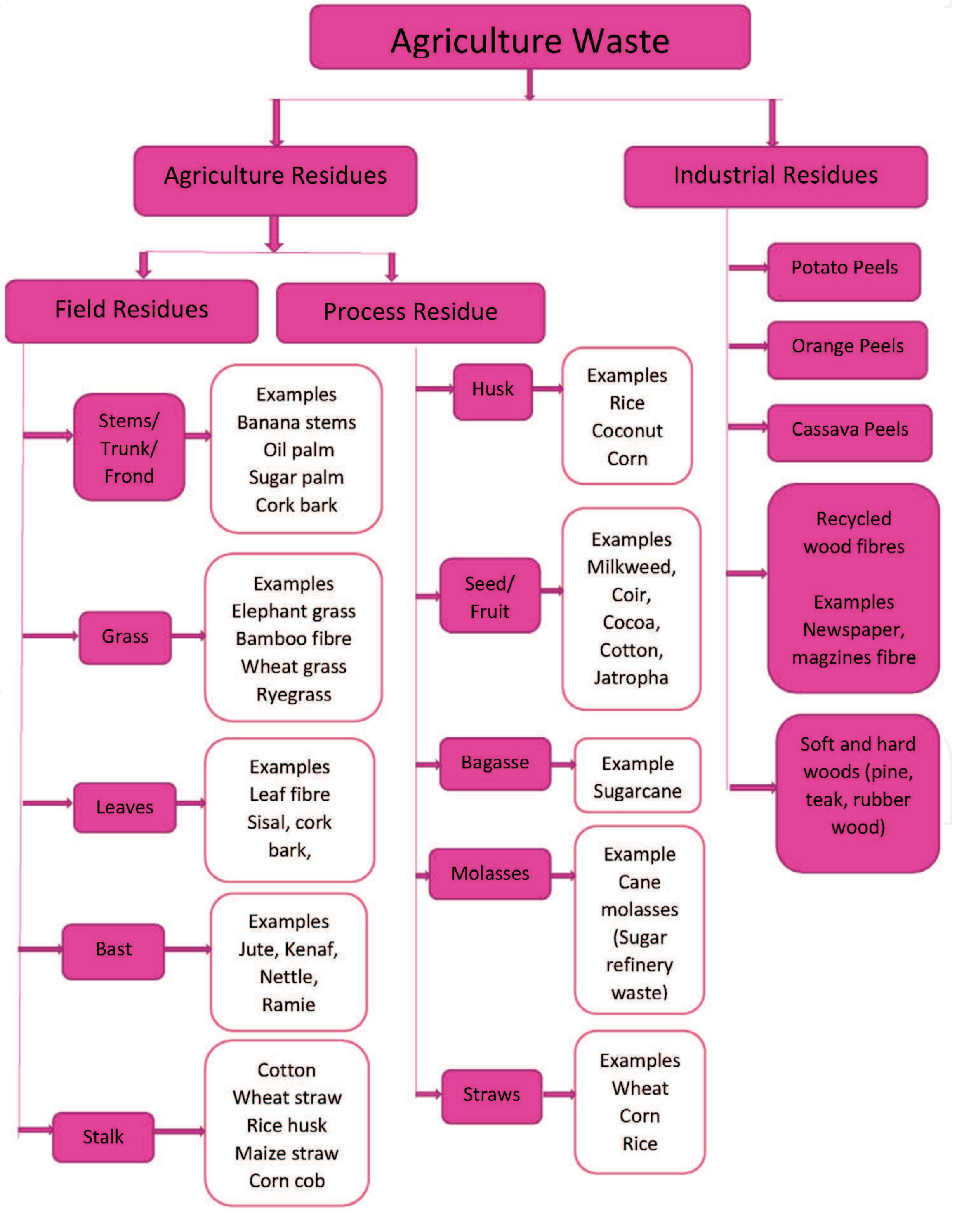

Figure 1.
Classification of agriculture waste based on source.

2.2 Industrial waste

We have millions of factories, mills, industries all around the world that use several types of raw materials to manufacture different type of products, goods, cosmetics, pharmaceuticals or other things. So, of course these all-manufacturing sites generate a vast amount of material which is rendered useless and called as 'Industrial waste'.

So, Industrial waste is defined as waste generated by manufacturing or industrial processes. The types of industrial waste generated include cafeteria garbage, dirt and gravel, masonry and concrete, scrap metals, trash, oil, solvents, biomass ash, discarded tires, chemicals, weed grass and trees, wood and scrap lumber, and similar wastes [8–12].

These all industrial wastes containing hazardous and nonhazardous components which either released into natural water bodies, or burnt or throw in open ground area without concerning about environmental elements. So, we can utilize all these wastes generated from small- or large-scale industries for so many applications or we can utilize all these scrapes by modification in chemical structures.

Saikia and Brito [9], reported the application of industrial waste as building material such as plastic waste in concrete, coal ash as an aggregate in concrete and rubber tire as a filler in concrete. He also enlightened on utilization of alloy slags in various applications. Dash et al. [13], reported a sustainable use of industrial waste as replacement of fine aggregate for the preparation of concrete. They utilize some industrial waste like foundry sand, steel slag, copper slag, furnace slag, coal bottom ash, ferrochrome slag, palm oil clinker etc. as a replacement of sand or aggregate in concrete. Aggarwal and Siddique [14], also utilize bottom ash and waste foundry sand as partial replacement of fine aggregates which gives us a fine option for substituting natural fine aggregate with industrial by-products. There are several studies in which industrial byproducts are used as adsorbent for the sorption of harmful dyes, pigments and heavy metals present in waste water streams. Anionic dyes such as ethyl orange, metanil yellow and acid blue removal were investigated by inorganic wastes such as blast furnace, sludge, slag from steel plants and by organic material prepared from carbon slurry of fertilizer. Various industrial waste or by-products produce by various industries are summarize in **Table 1**.

The use of agriculture waste as adsorbent towards many heavy metal ions are very well reported in various studies. The major chemical composition of agricultural residues with their properties and functions are depicted in **Figure 2**. Lignocellulosic biomass based on agriculture residues mainly composed of cellulose, lignin, hemicellulose, starch, ash etc. All these residues contain different percent composition of these components.

All the major components with their function and properties are shown in **Figure 2** and percent weight of these components consisted by different agriculture waste are shown in **Table 2** [15–18].

Huq et al. [19], efficiently transformed nanocrystalline cellulose (NCC) into reinforced alginate-based nanocomposite film. This study also gives a strong support for the utilization of agriculture waste as a rich source of biopolymer like cellulose. In this study NCC is prepared form wood pulp by acid hydrolysis and activated by treatment with sulfuric acid and then incorporated into nanoscalic alginate structure to produce a renewable and biodegradable film for food packaging applications.

All the agriculture wastes contain cellulose and hemicellulose as main part of its chemical structure, these all-agriculture residues are also referred as "Lignocellulosic mass". The cellulose and hemicellulose are polysaccharides which cover two-third part of the lignocellulosic biomass, which can be bioconverted in

S. N.	Industrial sector	Description	Typical waste
1.	Mining and quarrying	Extraction, beneficiation, and processing of minerals	Solid rock, slag, phosphogypsum, muds, tailings
2.	Energy	Electricity, gas, steam, and air-conditioning supply	Fly ash, bottom ash, boiler slag, particulates, used oils, sludge
3.	Manufacturing	Chemical	Spent catalyst, chemical solvents, reactive waste, acid, alkali, used oils, particulate waste, ash, sludge
4.	Food	Food	Plastic, packaging, carton
5.	Textile		Textile waste, pigments, peroxide, organic stabilizer, alkali, chemical solvents, sludge, heavy metals
6.	Construction	Construction, demolition activity	Concrete, cinder blocks, gypsum, masonry, asphalt, wood shingles, slate, metals, glass, and plaster
7.	Waste/water services	Water collection, treatment, and supply	Spent adsorbent, sludge

Table 1.
Industrial waste produced from various industries.

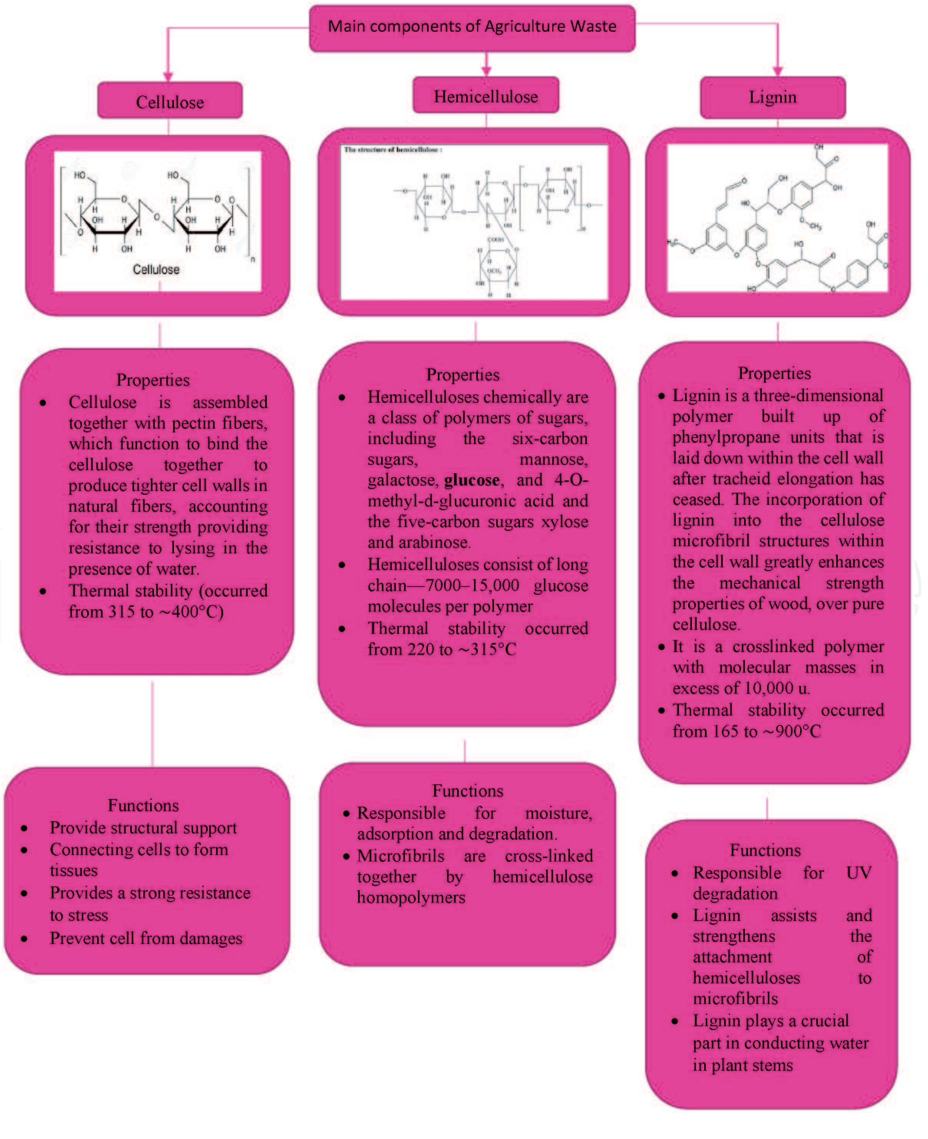

Figure 2.
Main components of agriculture waste.

S. N.	Agriculture residues	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)	Ash (wt%)
1.	Wheat Straw	43.2	34.1	22.0	1.8
2.	Sugar palm fiber	43.88	7.24	33.24	1.01
3.	Rice Husk	41.05	17.63	18.82	—
4.	Sugarcane bagasse	43.6	27.7	27.7	—
5.	Banana fiber	7.5	74.9	7.9	0.01
6.	Coconut husk	43.44	0.25	45.84	2.22

Table 2.
Percent composition of agriculture residues.

fermentable sugars like hexoses and pentoses under the action of cellulase enzymes. For this enzymatic hydrolysis is required and this rate of hydrolysis and cellulase enzyme activity is improved by presence of alginate. It enhances enzyme immobilization capacity which can further improve the stability and hydrolytic efficiency of cellulase. And the presence of Fe_3O_4/Alginate nanocomposite enhanced the production of reducing sugars from lignocellulosic mass – rice straw has also been shown by Srivastava et al. [20].

2.3 Lignocellulosic biomass

Lignocellulosic mass are the materials that contain cellulose as main content of its composition and rich in various nutrients. Agriculture waste are rich in cellulosic material so, these are also called as 'Lignocellulosic Biomass', as it is produced by various agro based industries. These materials are biodegradable neither toxic nor hazardous and have potential to play a vital role in various applications. Lignocellulosic Biomass' include organic wastes such as corncob, sugarcane bagasse, sugar palm (fiber, frond, bunch, trunk), areca nut husk fiber, wheat straw fiber, soy hull fiber, pineapple leaf fiber, oil palm (mesocarp fiber, empty fruit bunch, frond), rubber wood thinning, curaua fiber, banana fiber, water hyacinth fiber, wheat straw, sugar beet fiber, etc. (**Figure 3**). Lignocellulosic biomass in general consists of 35–55% cellulose, 25–40% hemicellulose, and 15–25% lignin with small percentage of extractives, protein, and ash [21].

2.4 Adsorption of heavy metal by alginate-based biopolymer nanocomposites

There are also so many studies have been reported in which alginate structure plays a very important role in order to enhance a adsorption capacity of synthesized material towards various organic, inorganic, Cationic, anionic environmental pollutants such as metal ion, dyes, phosphates, toluene, phenol, nitrates etc. various alginate structure based materials with their batch adsorption studies are summarized in **Table 3**. Lakouraj et al. reported an intense study on adsorption capacity of SA based nanogel and superparamagnetic nanocomposite. This study represents synthesis of novel, inexpensive, and eco-friendly nanobiosorbents namely, magnetic tetrasodium thiacalix [4] arene tetrasolfonate supported sodium alginate (TSTC [4] AS-s-SA) and utilized for sorption of Cu(II), Cd(II), Pb(II), Co(II), Ni(II) and Cr(II) [22]. Similarly, Mittal et al. [23], copolymerized alginate with methyl methacrylate magnetic nanocomposite for the sorption of Pb(II) and Cu(II) metal ions. Phiri et al. [24], fabricated novel magnetic nanocomposite alginate beads in which alginate beads impregnated with a new combination - bentonite, zeolite,

Figure 3.
Examples of lignocellulosic mass.

S. N.	Agro/industrial waste	pH	Other conditions	Adsorbates	Source
1.	Calcium alginate beads	6.0 to 7.0	25°C	Pb^{2+} and Cd^{2+}	[3]
2.	Tetrasodium thiacalix[4] arene tetrasulfonate (TSTC[4]AS-s-SA) nanogel	7	—	Cu(II), Cd(II), Pb(II), Co(II), Ni(II) and Cr(III)	[22]
3.	Poly (methyl methacrylate)-grafted alginate/Fe_3O_4 nanocomposite	5	50°C	Pb(II) and Cu(II)	[23]
4.	Alginate with bentonite, zeolite, activated charcoal and aluminum – zinc layered double hydroxides beads		—	Phosphate, copper, toluene	[24]
5.	Polyvinyl alcohol/sodium alginate (PVA/SA) beads	6.0 to 7.0		Pb^{2+}, Cd^{2+}, Sr^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+} and Li^{2+}	[25]
		5		Fe^{3+} and Al^{3+}	
6.	Cobalt ferrite - alginate nanocomposite	3–6	60 min	binary dye effluent	[26]
7.	Polyvinyl alcohol/graphene oxide-sodium alginate nanocomposite hydrogel		—	Pb^{2+}	[27]

Table 3.
Batch adsorption studies of various alginate-based biopolymer nanocomposite as adsorbent.

activated charcoal and aluminum – zinc layered double hydroxides was synthesized for removal of phosphate, copper and toluene with complete adsorption of these organic pollutants.

Karkeh-Abadi et al. [28], reported the synthesis of sodium alginate hydroxyapatite-CNT nanocomposite beads used as adsorbents of Cobalt ions from an aqueous solution. While Gokila et al. [29], show the performance of Chitosan and Alginate nanocomposites and proved as an excellent material for sequestration of Cr(VI) ions from waste water.

Enhancement in adsorption capacity by calcium alginate gel beads towards Pd(II) ion is also reported by Cataldo et al. [30]. In this study, two type of clay material Montmorillonite and Laponite utilized for synthesizing hybrid materials on the base of Ca-alginate.

The deprotonation of carboxylate ions present in alginate structure plays a very important role its enhanced binding ability with metal ions which in turn leads to greater adsorption capacity.

Esmat et al. [31], discussed alginate-based nanocomposites for the efficient removal of heavy metal ions. They prepared alginate-based nanocomposites by synthesizing cobalt ferrite nanoparticles (CF) and titanate nanotubes (T) and utilized as potential adsorbents for efficient removal of Cu^{2+}, Fe^{3+} and As^{3+} ions from water. This study shows that the presence of divalent cations such as Ca^{2+}, alginate transforms a gel form polymer matrix very easily which is easier to handle than powder materials and easily separable for desorption studies. The presence of alginates in nanostructures supports complex formation with metal ions present in aqueous solution which also increase its adsorption capacity to better extent.

Magnetic core shell nanoadsorbent using alginate base also have been coming forth as a possible option to remove organic and inorganic pollutants. Cobalt-ferrite nanoparticles embedded in alginate polymer matrix contain highly reactive surface and also allow fast magnetic separation after the adsorption process [26].

2.4.1 Silica based alginate bio-nanocomposite

There are various studies potrating silica as potential energy source for biofuels production, biochars, catalytic reforming, pollutant removal, soil remediation, waste water treatment and gas purification by means of adsorption, catalysis and another integrated process [32–34]. Nanoengineered Silica particles are widely used for biomedical purposes, in cosmetic products, food industry, automobiles, paints etc. Even rice husk silica waste is also used for the preparation of porous materials [35]. Waste material is a potential alternative source of silica. Extraction of silica from various agriculture as well as industrial waste are also very well reported [36–38]. Raja et al. [39], efficiently discussed the extraction methods of silica from agrowaste. Shen [34], enlightened various sustainable application for Rice husk silica derived nanomaterials. Sapawe et al. [40], synthesized silica from six different material as agriculture waste - sugarcane bagasse, bamboo culm, bamboo leaf, corncob, banana leaf and cigarette butt by sol gel method i.e., most common method to prepare polymeric network of gel. Salamaa et al. [41], crosslinked alginate with silica and zinc oxide in which silica is extracted from rice husk by conventional method and hybrid nano material is prepared by treating with alginate as matrix supporting material and investigated for antibacterial properties. However, adsorption property of silica alginate nanocomposites is not investigated yet but it has been shown former studies that alginate has played a very important role in enhancing the adsorption phenomena and as like alginate, silica also showed a potential adsorption capacity towards heavy metal ions. So, by combining these two compounds would result in a very efficient adsorbent nanocomposite material.

2.4.2 Carbon based alginate bio-nanocomposite

Carbon based nano adsorbents such as carbon nanotubes, graphene, nanodiamond, fullerenes, nanosized carbon allotropes have attracted tremendous interest for sorption of metal ion removal from wastewater due to their extraordinary performance with complete adsorption capacity and easy operational use but not low cost effective. By their chemical properties these derivatives contain high aspect ratios, surface areas, porosities and reactivities. Moreover, they exhibit high electrical and thermal conductivity, great mechanical property and structural stability in extreme conditions such as high temperature, strong acidic/alkaline conditions. Due to their high hydrophobicity and small sized, it is difficult to recollect from aqueous solution. To overcome such disadvantages, many studies had been reported to modify chemical structures by grafting with biopolymeric network [42]. Yu et al. [27], prepared polyvinyl alcohol/graphene oxide-sodium alginate nanocomposite hydrogel through in situ crosslinking for Pb^{2+} removal which reveals that intercalation of GO structure in alginate based polymeric network increase metal ion complexation because of its abundant functional groups, such as hydroxyl, carboxyl, carbonyl, and epoxy groups on the surfaces. Similarly, Karkeh-Abadi et al. [28] incorporated functionalized CNT in the network of sodium alginate-based nanocomposite beads on the removal of Co(II) ions from aqueous solutions. Here, CNTs are promising synthetic polymers because of their large surface area, greater chemical reactivity, high aspect ratio, less chemical mass and impact on the environment. Yadav et al. [43] fabricated Novel Magnetic/Activated Charcoal/β - Cyclodextrin/Alginate Polymer Nanocomposite and utilized for elimination of methylene blue dye. As activated charcoal has been used as a common "universal" adsorbent, since it is a simple, safe, high surface area and high adsorption capacity material. Konwar and Chowdhury [44] studies property relationship of alginate and alginate carbon dots nanocomposite with different bivalent and trivalent metal ions such as - Ca^{2+}, Ba^{2+}, Cu^{2+}, Fe^{3+} and Al^{3+}. Carbon dots were prepared from 'Assam Tea' and improved the properties like UV blocking, thermostability and mechanical strength of these prepared biopolymeric films. Ma et al. [45] reported enhanced adsorption for removal of antibiotics by carbon nanotubes/graphene oxide/sodium alginate triple-network nanocomposite hydrogels in aqueous solutions.

All these above studies incorporated carbon derivatives with alginate structure and resultant material were utilized for adsorption of metal ions in different forms. Agriculture as well as industrial waste are also key source of carbon derivatives. Various studies have been reported in which these carbon derivatives are extracted from agriculture/industrial residues. Mohan et al. [46], develop activated carbon from coconut shell for removal of pyridine derivatives. Kerdnawee et al. [47] discussed the advancement of carbonaceous nanomaterial production from industrial waste in detail. This study enlightened several studies reported for synthesis of CNT using industrial waste such as – chemical process waste, petroleum refining process waste, plastic waste, automobile waste, because these wastes contains high amount of CH4, C_2H_6, C_2H_4, C_2H_2, CO, CH_3OH and so on, would involve as carbon source for productions of carbonaceous material. Somanathan et al. [48] reported graphene oxide synthesis via single step reforming of sugar cane bagasse. It is green approach for synthesis of GO. There is also another review study which is reported for production of activated carbon from agriculture waste. This detailed study is collection of various studies based for production of activated carbon from agriculture waste such as – pineapple peels, rice husks, cotton stalk, orange peel, tobacco stems, bamboo, waste tea, industrial waste lignin, pine wood powder etc., by microwave method [49]. Ensuncho-Muñoz and Carriazo [50], reported for e preparation and characterization of carbonaceous materials obtained from three types of vegetable wastes provided by agricultural industries i.e.; coconut husk, corn cob and rice husk and utilized as adsorbent of azo dyes.

So, from all the above studies we can conclude that carbonaceous material can be produce from agriculture as well as industrial waste. I also reported for the studies based on preparation of alginate nanocomposites with different form of carbonaceous materials. So these studies evident that carbon based alginate nanocomposites can be synthesized by utilizing agriculture and industrial waste. There are also various methods like sol gel method, microwave heating method, modified hummers method, calcination method, grafting and copolymerization reaction with the help of crosslinkers are also come into consideration for preparation. Of course, no study has been found to be reported which involve direct linkage between alginate with carbonaceous derivatives obtained from agriculture/industrial waste and utilized for removal of heavy metals from wastewater, so there is research gap but definitely it could result into a very efficient adsorbent material.

3. Conclusion

So, utilization of alginate as biopolymer in nanocomposites is beneficial from every side of its applications. It is biodegradable, biocompatible, renewable, nontoxic and moderately efficient. That is why it contains numerous applications in biomedical science and engineering, agriculture, drug delivery, enzyme mobilization, heavy metal removal from industrial effluents, as functional food ingredient, mineralization of organic pollution, emulsifiers, consistency enhancers, and thickening agents in cosmetic formulas etc. Limited studies are reported for combination of alginate with industrial/agriculture waste in nanoscalic material so far, but this review study enlightening the several studies based on nanocomposite combination of alginates and biopolymers and these biopolymers can also be derived from various agro/industrial waste by simple chemical and mechanical methods. So, we should work on the formulation of alginates agro/industrial waste nanocomposites. Preparation of alginate nanomaterials with agriculture/industrial waste constituents confirms its effectiveness in water purification. In the environment, we can control its reutilization by desorption studies. Another advantage is that it can be transform from nanoparticles to nano polymeric films and support to batch adsorption process to fixed bed column in form of large-scale application. Apart from that utilization of biological materials as adsorbents for elimination of pollutants minimize the process price substantially and make adsorption method more ecological and feasible.

Author details

Shivangi Omer
School of Applied and Life Sciences, Uttaranchal University, Dehradun, India

*Address all correspondence to: shivangiomer@gmail.com

References

[1] Lee, K. Y, Mooney, D. J : Alginate: properties and biomedical applications. Progress in polymer science. 2012; *37*(1):106-126.

[2] Pereira, L., & Cotas, J. Introductory Chapter: Alginates-A General Overview. Alginates-Recent Uses of This Natural Polymer: intechopen; 2020. DOI: 10.5772/intechopen.88381

[3] Alfaro-Cuevas-Villanueva, R., Hidalgo-Vázquez, A. R., Cortés Penagos, C. D. J., Cortés-Martínez, R. Thermodynamic, kinetic, and equilibrium parameters for the removal of lead and cadmium from aqueous solutions with calcium alginate beads. The scientific world journal, 2014.

[4] Obi, F. O., Ugwuishiwu, B. O., & Nwakaire, J. N. Agricultural waste concept, generation, utilization and management. Nigerian Journal of Technology. 2016*; 35*(4):957-964.

[5] Sadh, P. K, Duhan, S, & Duhan, J. S. Agro-industrial wastes and their utilization using solid state fermentation: a review. Bioresources and Bioprocessing. 2018; *5*(1): 1.

[6] Omer, S., Singh. A. and Upadhyay S. Synthesis of Chitosan-g-Biomass Ash/Graphene Oxide Nanocomposite for the Removal of Copper and Chromium from Industrial Waste Water. Clay Research. 2019[a]; *38*(1):19-28.

[7] Omer, S., Singh, A., Sasmal, R., & Singhal, A. Adsorption studies on chitosan and guar gum nanocomposite by application of agriculture waste–A review. International Journal of Research and Analytical Reviews 2019[b];*6*: 1059-1062.

[8] Mittal, A., Ahmad, R., & Hasan, I. Poly (methyl methacrylate)-grafted alginate/Fe3O4 nanocomposite: synthesis and its application for the removal of heavy metal ions. Desalination and Water Treatment. 2016; 57(42): 19820-19833.

[9] Saikia, N., & de Brito, J. (2009). Use of industrial waste and municipality solid waste as aggregate, filler or fiber in cement mortar and concrete. Advanced Material Science and Research. 2009; *3*: 65-116.

[10] Singh, A. and Omer. S. Adsorption of Heavy metal using Biomass ash and Guar gum Nanocomposite from waste water effluent – A review', SSRN- Elsevier. 2018; 1: 3.

[11] Omer, S., Anand, S., Singh, S. K., Singh, A. Review Study on Waste Tire as an Adsorbent to Remove Toxic Metals from Waste Water. International Journal of Pharmaceutical and Medicinal Research*. 2020; 8*(1): 1-5.

[12] Omer, S. & Singh, A. Synthesis of Guar Gum -g-Coconut husk (SnO_2-SiO_2) Nanocomposite For Removal of Cu(II) and Cr(VI) From Waste Water. International Journal of Environment and Waste Management. 2022 (in press); 1(1): 1. DOI:10.1504/ijewm.2022.10036122.

[13] Dash, M. K., Patro, S. K., & Rath, A. K. Sustainable use of industrial-waste as partial replacement of fine aggregate for preparation of concrete–A review. International Journal of Sustainable Built Environment. 2016; 5(2): 484-516

[14] Aggarwal, Y., & Siddique, R. Microstructure and properties of concrete using bottom ash and waste foundry sand as partial replacement of fine aggregates. Construction and Building Materials. 2014; 54: 210-223.

[15] Faisal, Z. T., Amri, F., & Tahir, I. (2010). Effect of maleic anhydride polypropylene on the properties of coconut shell filled thermoplastic elastomeric olefin composites. Indonesian Journal of Chemistry. 2010; 10(2): 156-161.

[16] Verma, D., & Gope, P. C. The use of coir/coconut fibers as reinforcements in composites. In Biofiber Reinforcements in Composite Materials. 2015: 285-319.

[17] Gregory, A. and Bolwell, G.P. Hemicelluloses. Comprehensive Natural Products Chemistry. 1999; 3: 599-615.

[18] Tian, S. Q., Zhao, R. Y., & Chen, Z. C. Review of the pretreatment and bioconversion of lignocellulosic biomass from wheat straw materials. Renewable and Sustainable Energy Reviews. 2018; 91: 483-489.

[19] Huq, T., Salmieri, S., Khan, A., Khan, R. A., Le Tien, C., Riedl, B., ... & Lacroix, M. Nanocrystalline cellulose (NCC) reinforced alginate based biodegradable nanocomposite film. Carbohydrate polymers. 2012; 90(4): 1757-1763.

[20] Srivastava, N., Singh, J., Ramteke, P. W., Mishra, P. K., & Srivastava, M. Improved production of reducing sugars from rice straw using crude cellulase activated with Fe3O4/Alginate nano-composite. Bioresource technology. 2015; 183: 262-266.

[21] Ilyas, R. A., Sapuan, S. M., Ibrahim, R., Atikah, M. S. N., Atiqah, A., Ansari, M. N. M., & Norrrahim, M. N. F. Production, processes and modification of nanocrystalline cellulose from agro-waste: a review. Nanocrystalline materials. 2019: 3-32.

[22] Lakouraj, M. M., Mojerlou, F., & Zare, E. N. Nanogel and super-paramagnetic nanocomposite based on sodium alginate for sorption of heavy metal ions. Carbohydrate Polymers. 2014; 106: 34-41.

[23] Mittal, A., Ahmad, R., & Hasan, I. Poly (methyl methacrylate)-grafted alginate/Fe3O4 nanocomposite: synthesis and its application for the removal of heavy metal ions. Desalination and Water Treatment. 2016; 57(42): 19820-19833.

[24] Phiri, I., Ko, J. M., Mushonga, P., Kugara, J., Onani, M. O., Msamadya, S., ... & Madzvamuse, A. Simultaneous removal of cationic, anionic and organic pollutants in highly acidic water using magnetic nanocomposite alginate beads. Journal of Water Process Engineering. 2019; *31*: 100884.

[25] Isawi, H. (2020). Using zeolite/polyvinyl alcohol/sodium alginate nanocomposite beads for removal of some heavy metals from wastewater. Arabian Journal of Chemistry. 2020; 13(6): 5691-5716.

[26] Jayalakshmi, R., & Jeyanthi, J. Simultaneous removal of binary dye from textile effluent using cobalt ferrite-alginate nanocomposite: Performance and mechanism. Microchemical Journal. *2019*; *145*: 791-800.

[27] Yu, Y., Zhang, G., & Ye, L. Preparation and adsorption mechanism of polyvinyl alcohol/graphene oxide-sodium alginate nanocomposite hydrogel with high Pb (II) adsorption capacity. Journal of Applied Polymer Science. 2019; 136(14): 47318.

[28] Karkeh-Abadi, F., Saber-Samandari, S., & Saber-Samandari, S. The impact of functionalized CNT in the network of sodium alginate-based nanocomposite beads on the removal of Co (II) ions from aqueous solutions. Journal of hazardous materials. 2016; *312*: 224-233.

[29] Gokila, S., Gomathi, T., Sudha, P. N., & Anil, S. Removal of the heavy metal ion chromiuim (VI) using Chitosan and Alginate nanocomposites. International journal of biological macromolecules. 2017; 104: 1459-1468.

[30] Cataldo, S., Muratore, N., Orecchio, S., & Pettignano, A. Enhancement of adsorption ability of calcium alginate gel beads towards Pd (II) ion. A kinetic and equilibrium study on hybrid Laponite and Montmorillonite–alginate gel beads. Applied Clay Science. 2015; 118: 162-170.

[31] Esmat, M., Farghali, A. A., Khedr, M. H., & El-Sherbiny, I. M. (2017). Alginate-based nanocomposites for efficient removal of heavy metal ions. International journal of biological macromolecules, *102*, 272-283.

[32] Zhong, R., Yu, F., Schutyser, W., Liao, Y., de Clippel, F., Peng, L., & Sels, B. F. Acidic mesostructured silica-carbon nanocomposite catalysts for biofuels and chemicals synthesis from sugars in alcoholic solutions. Applied Catalysis B: Environmental. 2017; 206: 74-88.

[33] Budhi, S., Mukarakate, C., Iisa, K., Pylypenko, S., Ciesielski, P. N., Yung, M. M., ... & Trewyn, B. G. Molybdenum incorporated mesoporous silica catalyst for production of biofuels and value-added chemicals via catalytic fast pyrolysis. Green Chemistry. 2015; *17*(5): 3035-3046.

[34] Shen, Y. Rice husk silica derived nanomaterials for sustainable applications. Renewable and Sustainable Energy Reviews. 2017; 80: 453-466.

[35] Elimbinzi, E., Nyandoro, S. S., Mubofu, E. B., Manayil, J. C., Lee, A. F., & Wilson, K. Valorization of rice husk silica waste: organo-amine functionalized castor oil templated mesoporous silicas for biofuels synthesis. Microporous and Mesoporous Materials. 2020; 294: 109868.

[36] Anuar, M. F., Fen, Y. W., Zaid, M. H. M., Matori, K. A., & Khaidir, R. E. M. Synthesis and structural properties of coconut husk as potential silica source. Results in Physics. 2018; *11*: 1-4.

[37] Naqvi, J., Shah, F. H., & Mansha, M. Extraction of amorphous silica from wheat husk by using KMnO4. Journal of faculty of engineering & technology. 2011; 18(1): 39-46.

[38] Osman, N. S., & Sapawe, N. Waste material as an alternative source of silica precursor in silica nanoparticle synthesis–a review. Materials Today: Proceedings. 2019;19: 1267-1272.

[39] Raja, S. A Review: Sources of Silica from Agro Waste and Its Extraction Methods JARDCS. 2019; 11: 765-772.

[40] Sapawe, N., Surayah Osman, N., Zulkhairi Zakaria, M., Amirul Shahab Syed Mohamad Fikry, S., & Amir Mat Aris, M. Synthesis of green silica from agricultural waste by sol-gel method. Materials Today: Proceedings. 2018; 5(10): 21861-21866. DOI:10.1016/j.matpr.2018.07.043

[41] Salama, A., Diab, M. A., Abou-Zeid, R. E., Aljohani, H. A., & Shoueir, K. R. Crosslinked alginate/silica/zinc oxide nanocomposite: a sustainable material with antibacterial properties. Composites Communications. 2018; 7: 7-11.

[42] Yu, G., Lu, Y., Guo, J., Patel, M., Bafana, A., Wang, X., ... & Wujcik, E. K. Carbon nanotubes, graphene, and their derivatives for heavy metal removal. Advanced Composites and Hybrid Materials. 2018; 1(1): 56-78.

[43] Yadav, S., Asthana, A., Chakraborty, R., Jain, B., Singh, A. K., Carabineiro, S. A., ... & Hassan, A. B. Cationic dye removal using novel magnetic/activated charcoal/β-cyclodextrin/alginate polymer nanocomposite. Nanomaterials. 2020; 10(1): 170.

[44] Konwar, A., & Chowdhury, D. Property relationship of alginate and alginate–carbon dot nanocomposites with bivalent and trivalent cross-linker ions. RSC Advances. 2015; 5(77): 62864-62870.

[45] Ma, J., Jiang, Z., Cao, J., & Yu, F. Enhanced adsorption for the removal of antibiotics by carbon nanotubes/graphene oxide/sodium alginate triple-network nanocomposite hydrogels in aqueous solutions. Chemosphere. 2020; 242: 125188.

[46] Mohan, D., Singh, K. P., Sinha, S., & Gosh, D. Removal of pyridine

derivatives from aqueous solution by activated carbons developed from agricultural waste materials. Carbon. 2005; 43(8): 1680-1693.

[47] Kerdnawee, K., Termvidchakorn, C., Yaisanga, P., Pakchamsai, J., Chookiat, C., Eiad-Ua, A., ... & Charinpanitkul, T. Present advancement in production of carbon nanotubes and their derivatives from industrial waste with promising applications. KONA Powder and Particle Journal. 2017: 2017001.

[48] Somanathan, T., Prasad, K., Ostrikov, K. K., Saravanan, A., & Krishna, V. M. Graphene oxide synthesis from agro waste. Nanomaterials. 2015; 5(2): 826-834.

[49] Hesas, R. H., Daud, W. M. A. W., Sahu, J. N., & Arami-Niya, A. The effects of a microwave heating method on the production of activated carbon from agricultural waste: A review. Journal of Analytical and Applied pyrolysis. 2013; 100: 1-11.

[50] Ensuncho-Muñoz, A. E., & Carriazo, J. G. Characterization of the carbonaceous materials obtained from different agro-industrial wastes. Environmental technology. 2015; 36(5): 547-555.