



Recent advances in alginate-based adsorbents for heavy metal retention from water: a review

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ABSTRACT

Heavy metal pollution has become a major environmental concern because modern industries produce heavy metals in their effluents. Adsorption is regarded as an environmentally friendly way to clear industrial effluents from heavy metals because of its simplicity and low cost. As a natural polysaccharide containing abundant hydroxyl and carboxyl groups, sodium alginate has been widely reported to be a useful raw material for the adsorption of heavy metals from aqueous solutions. Alginate-based materials have been limited in their industrial application because of their poor physical strength and thermostability. However, adsorbents synthesized from sodium alginate exhibit large uptake capacities as well as high removal rates of heavy metal ions following surface grafting and cross-linking. Specifically, this paper summarizes the development of sodium alginate-based composite materials, including their polymeric properties, modification, and their adsorption behaviors. The work investigated the adsorption mechanisms of different alginate-based composites for the removal of heavy metals such as Cu(II), Pb(II), and Cd(II). Alginate-based composites typically exhibit enhanced adsorption performance. The physical and chemical properties of alginate-based composites determine their effectiveness under different application conditions. A series of alginate-based composites and their physicochemical and adsorptive properties have been summarized. Finally, the limitations of sodium alginate-based adsorbents were discussed along with suggestions for future research.

Keywords: Alginate composites; Adsorption; Metal ion removal; Functionalization

1. Introduction

Water is a basic necessity in existence and is necessary to all living things; hence rising demand and scarcity of pure water sources have become key concerns in recent years. Global population increase and intensive residential activities, as well as the development of industrial

and agricultural activities, have knowingly released huge amounts of harmful chemicals into water systems, particularly in developing nations. Improper treatment of industrial effluents containing moderate levels of metallic cations will result in other problems for human health and the environment [1]. Toxic compounds are dissolved in water or deposited on the bed when they enter water

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bodies. As a result, water quality deteriorates, posing a threat to aquatic ecosystems. Heavy metals are more pronounced than other types of contaminants due to their continual accumulation, high toxicity, and high permeability [2]. Heavy metal pollution of water is typically associated with effluents from industries such as mining [3], metal plating [4], tanneries [5], batteries [6], pesticides [7], fertilizer [8], and paper industries [9]. Because the dangers of exposure to these contaminants are widely established, their occurrence in water bodies above a particular threshold can be harmful to human health and ecosystem stability. To date, numerous remediation technologies including membrane filtration [10], flocculation [11], and coagulation [12] have been identified as possible solutions for heavy metals removal from water. To eliminate these inorganic hazardous substances from water and wastewater, methods such as precipitation, adsorption, reverse osmosis, advanced oxidation processes, ion exchange, electrochemistry, photocatalysis, and biological treatment have been developed [13,14]. Because of its simplicity of design, extensive applicability, cost-effectiveness, and feasibility, adsorption is often regarded as the most promising approach for water purification and separation [15–17]. The efficiency and cheap treatment cost are the most significant characteristics of an excellent adsorbent [18]. As a result, a wide range of materials, including activated carbon, have been proposed and explored for their potential [19], natural polymers [20], carbon nanotubes [21], zeolites [22], clays [23], and biochar [24]. In terms of abundance, renewability, economics, and selectivity to pollutants, the creation of adsorbents from natural polymers such as alginate has been one of the most promising solutions for decades. Sodium alginate is a nontoxic, biodegradable linear biopolymer that is high in carboxyl and hydroxyl groups. Alginate is a natural polymer derived from brown algae that have intriguing properties such as being non-toxic, biodegradable, and biocompatible. It also has a high concentration of carboxyl and hydroxyl groups along its polymer structure, making it the greatest choice for removing heavy metals and radionuclides from aqueous solutions [20,25]. Alginate has been widely employed as an adsorbent with high adsorption efficiency, as well as being functionalized with other materials to overcome its limitations and improve removal performance [26]. Alginate can generally be added to composite materials like interpenetrating polymer networks, networks made through grafting polymerization [27], nanocomposites made from materials derived from carbon [28,29], and nanocomposites made from natural nanomaterials to create advanced adsorbents [30].

Despite the enormous body of research, there are only a few papers on alginate composites for heavy metals that cover the creation of the polymer, particular test settings, reaction parameter influence, and mechanisms in the adsorption process. The primary goal of this review is to give a summary of information on the advancement of alginate-based composites and their modifications as heavy metal adsorbents in aqueous media. To do so, researchers' findings are scrutinized to determine the efficacy of alginate and its composites in certain applications. The removal of metal ions from wastewater becomes more cost-effective when the adsorbent is reused for longer periods. Heavy

metal ions interact with homopolymers, copolymers, blends, or composites containing anions or electron-rich groups in a variety of ways, including π -interactions, dipole-dipole interactions, hydrogen bonding, or van der Waals force. Adsorption kinetics and isotherms are used to study the adsorption process. The adsorption behavior of different alginate composites is discussed in this article. The adsorption performance findings are compared and discussed in detail. In addition, some relevant information about crucial adsorbent characteristics is offered to stimulate the development of ideas. There are four primary parts to this review. The general introduction and qualities of alginate are discussed first. The use of alginate-based adsorbents for the removal of various metals, as well as important parameters such as pH, adsorbent dosage, metal ion concentration, contact time, temperature, and co-existing ions, are summarized. Thermodynamic parameters, adsorption isotherm models, and adsorption mechanisms are also explored. The review gives an overview of heavy metal removal research using alginate-based adsorbents, covering future directions and important challenges or limitations in the present body of research. Finally, we outlined the limitations of existing research, identified certain knowledge gaps, and proposed some potential fixes for sodium alginate-based adsorbents.

2. Physicochemical characteristics of alginate

Alginate is a polysaccharide that is found in abundance in nature. It comes from two different sources: algae and bacteria. Alginate's major component is alginic acid, while sodium alginate is a sodium salt of alginic acid. The most common form of commercial alginate is salt, which is commonly produced from brown algae (Phaeophyceae) using aqueous alkali solutions (NaOH). *Laminaria hyperborea*, *Macrocystis pyrifera*, and *Ascophyllum nodosum* are among the algae species found here. Bacteria such as *Azotobacter* and *Pseudomonas* species can also create alginate. Microbial fermentation may yield alginate with more specified physicochemical features; however, it is not cost-effective for commercial use and is limited to small-scale research projects [31,32].

Alginate is a linear, unbranched polysaccharide made up of 1,4-glycosidic linkages connecting-mannuronic acid (M) and guluronic acid (G) residues (Fig. 1). The residues are organized in a block pattern along the chain and vary greatly in composition and sequence. Haug and Larsen [33] described the chemical structure of this biopolymer as early as the 1960s. After partial acid hydrolysis, alginate was decomposed into three components, according to them. Two of these compositions are made up of nearly homo-polymeric M (M-block) and G (G-block) molecules, respectively, while the third is made up of a large number of alternating MG residues (MG-block).

Calcium alginate (CAI) hydrogel with the same morphology and structure may be easily generated in large quantities using proper cross-linking of the NNS-Alg hydrogel and Ca(II) ions, and the durability of the 3D network nanostructures in aqueous solution is increased (Fig. 2).

3. Functionalized alginate adsorbents

Heavy metal waste, which is dangerous to the environment, is produced in vast quantities by industry. Contamination

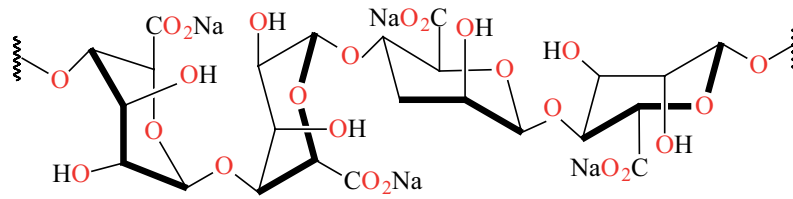


Fig. 1. Chemical structure of sodium alginate.

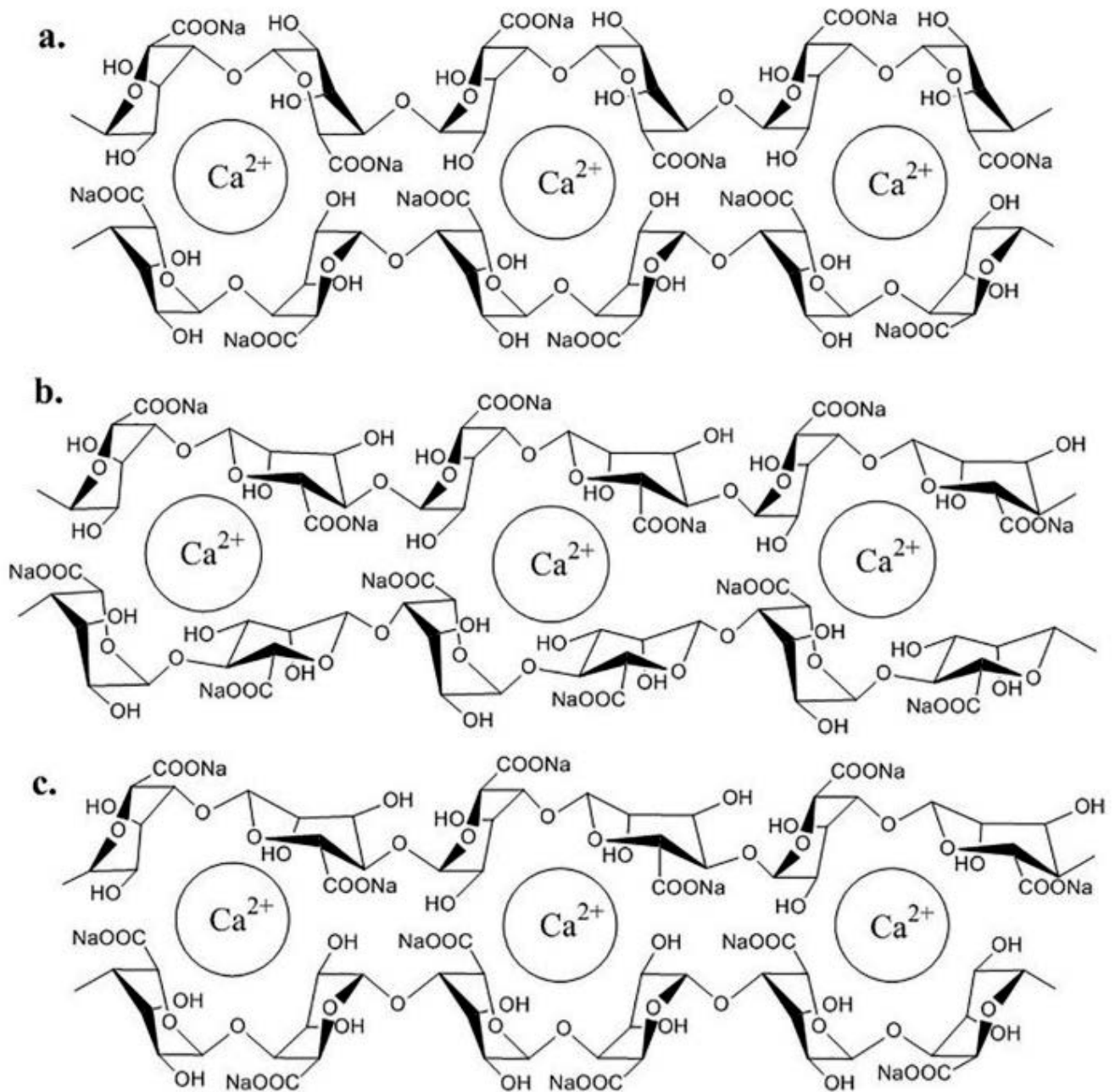


Fig. 2. Alginate binding points: (a) GG/GG, (b) MG/MG, and (c) GG/MG.

of water bodies with hazardous heavy metals is a major concern in many countries. Copper, cadmium, and lead are the two most common hazardous metals found in aquatic ecosystems as a result of their widespread use in a variety of sectors for a variety of purposes, therefore must be removed from wastewater. Biosorption, which is the adsorption of metal ions by biomaterials such as polysaccharides, is one of the most often used methods. Polysaccharide homopolymers, polysaccharide blends, copolymers, and polysaccharide composites are divided into four types in this review. Natural polysaccharides have several functional groups, such as chitin, chitosan, cellulose, starch, and alginate. To make it more efficient for heavy metal ion adsorption, extra functionalization is added in the form of blending, grafting, or combining different nanomaterials with additional functional groups. The addition of a second component to the primary polymer chain not only adds functionality, but it also improves mechanical strength, which is one of the most important needs for adsorbent recyclability. For example, Yadav et al. [34] described the modification of alginate by free radical polymerization of 2-acrylamidoglycolic acid in an inert atmosphere employing an efficient potassium peroxydiphosphate/silver nitrate redox system. The reaction conditions for maximum grafting have been optimized by varying reaction variables such as the concentration of 2-acrylamidoglycolic acid (20–73 mmol/L), potassium peroxydiphosphate (4–20 mmol/L), silver nitrate (1.2–4.4 mmol/L), sulphuric acid (1–8 mmol/L), alginate (0.4–1.8 g/L), time duration. The thermal data show that the synthesized graft copolymer is thermally more stable than pure alginate. The synthesized graft copolymer, that is, alginate-g-2-acrylamidoglycolic acid shows better results for swelling, and flocculating properties in comparison to alginate, this could be interpreted as the graft copolymer shows the enhancement in these properties. The spectroscopic data confirm that the grafting of 2-acrylamidoglycolic acid might have taken place in the hydroxyl group, which is supported by a tentative mechanism suggested for grafting. The thermal analysis data show that graft copolymer, a hybrid material in which properties of monomer are added by grafting, could be exploited very well industrially [34].

In a different investigation, Ni(II) and Zn(II) metal ions from an aqueous solution were adsorbed using alginate beads made of alginate-biuret and alginate-urea (in single and in the bimetallic component solution) [35]. ESEM-EDX was used to examine the synthesized adsorbents' characteristics. The modeling of experimental data shows that the PSORE equation fits the kinetic profiles well, while the results of the sorption isotherms correspond well to the Langmuir and Sips models (heterogeneous surface). Thermodynamic research also proved that adsorption is an endothermic process and is spontaneous. Alginate, alginate-biuret, and alginate-urea beads had maximum adsorption capacities of 3.22, 4.73, and 8.53 mmol/g for Ni(II), respectively, whereas Zn(II) had maximum adsorption capacities of 6.77, 6.97, and 7.14 mmol/g for alginate, alginate-biuret, and alginate-urea, respectively. The results showed that while Ni(II) ions were concentrated/enriched in the solution in the case of alginate-urea, Zn(II) was selectively adsorbed at 0.3 mmol/L concentration, but alginate-biuret and alginate beads absorbed about the same amount

of Ni(II) and Zn(II). The analysis of selectivity coefficients in the bimetallic solution demonstrates that alginate-urea is a selective sorbent for Zn(II) ions and alginate-biuret for Ni(II) ions [35]. Nickel and zinc ions were characterized by scanning electron microscopy (SEM) on an alginate-based sorbent. It was discovered that the bulky particles are present on the surface of Zn(II)-loaded biomass while comparing micrographs of alginate-urea-Zn(II)-loaded, alginate-urea-Ni(II)-loaded, and alginate-urea unloaded. In addition, the pores become dark.

The combination of polyethylenimine with alginate produces highly percolating membranes (with glutaraldehyde crosslinking) [36]. The macroporous structure of the material was shown via SEM. Before and after Cr anions sorption, the material is evaluated using FTIR. Batch-simulated continuous sorption tests found that maximal sorption occurred at pH 2, and the flow rate has only a minor impact on sorption efficiency. The PSORE and Sips equations, respectively, fit uptake kinetics and sorption isotherms well. The maximum sorption is at 314 mg/g. To assess sorbent selectivity, competition effects from Ca(II), Cu(II), Cl, NO₃⁻, and SO₄²⁻ are explored. The membranes are used to treat a Cr(VI)-contaminated electroplating wastewater simulation. Successive cycles of sorption and desorption show that the membranes maintain adsorption capacity higher than 200 mg/g for both Cr(VI) and total chromium for the first two cycles [36].

In another study, Eric Guibal team functionalized alginate/algal composite with polyethylenimine and then characterized using SEM (Fig. 3) [37]. After metal ion adsorption at pH 2, the adsorbent bead surface exhibits some degree of abrasion. On the one hand, it is partly a result of the ongoing shaking process, but on the other, the association of metal ions with the functional groups of the adsorbent (either externally or internally) may result in the disruption of the bead's homogenous structure. When metal ions are added, the internal pore structure of the adsorbent bead is scarcely changed compared to the original adsorbent bead, according to cross-section micrographs [37].

Originally, the alginate/PEI (Alg-PEI) sorbent, which consisted of calcium alginate (as an encapsulating matrix) and polyethylenimine derivatives, was made by internal ionotropic gelation and evaluated in batch and continuous systems [38]. The addition of *Fucus vesiculosus* alga improved this material by partially replacing the industrial alginate in the adsorbent; it also provided a practical one-pot process for faster fabrication and allowed the creation of a novel environmentally friendly material (alginate/*Fucus vesiculosus*/PEI; Alg-F-PEI). The PSORE was used to describe the uptake kinetics data, and the Langmuir, Freundlich, and Sips equations were used to fit the sorption isotherms. The Sips model provided a better description of the experimental data, and the sorption capacities were ordered as follows: For Alg-PEI, Pb(II)Cu(II) > Cd(II) Ni(II) > Zn(II) and Cu(II) > Pb(II) > Zn(II)Ni(II) > Cd(II) for Alg-F-PEI. Alg-F-PEI material had the highest sorption capacities for heavy metal removal (1.44 mmol/g for Cu(II); 1.09 mmol/g for Pb(II); 1.03 mmol/g for Ni(II); 1.07 mmol/g for Zn(II); and 0.87 mmol/g for Cd(II) at pH 4). The sorbents were recycled in a 0.1 M HCl/0.05 M CaCl₂ solution; the materials had higher selectivity for Pb(II) and

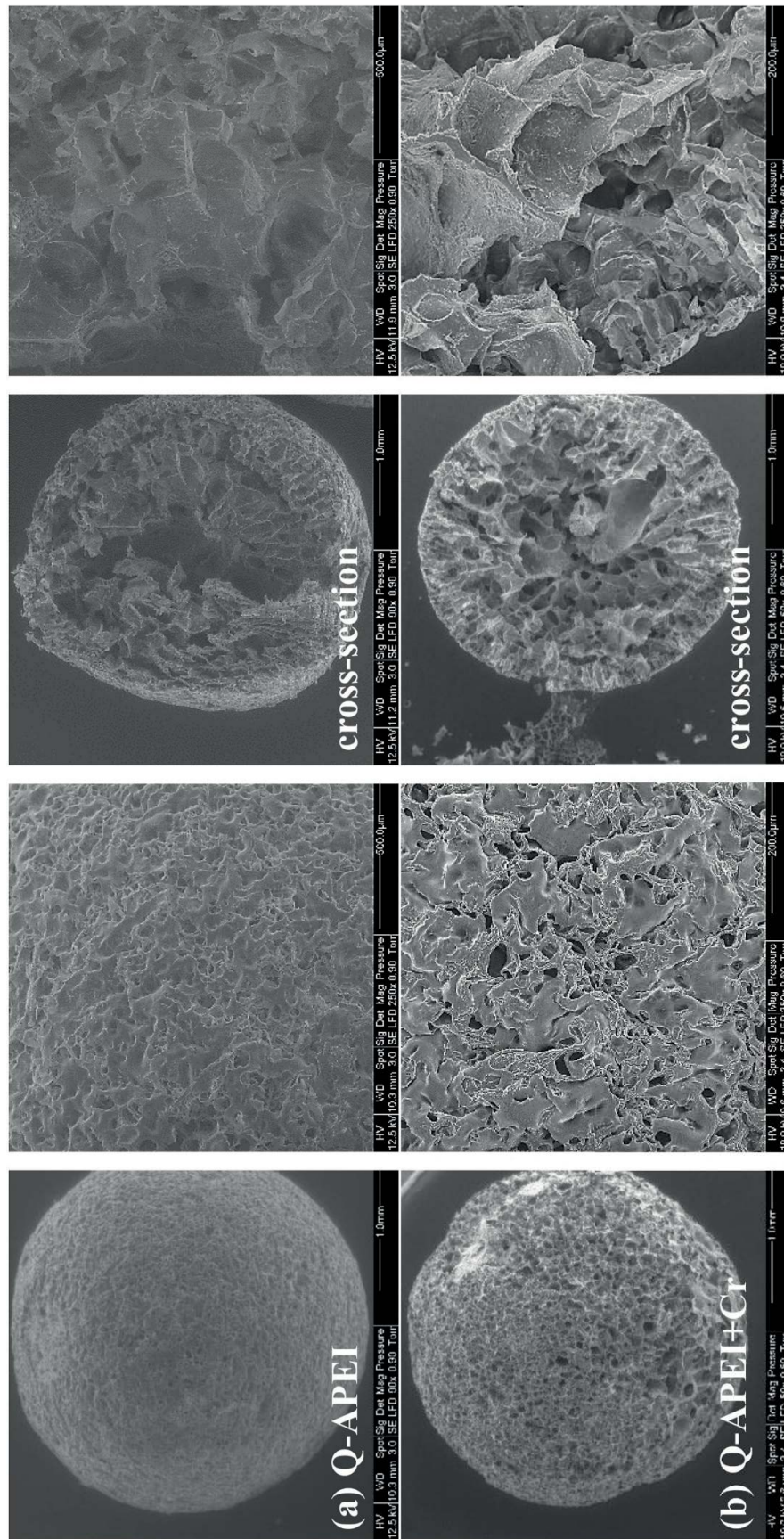


Fig. 3. SEM micrographs of surface and corresponding cross-section of algal/alginat-polyethylenimine beads before and after metal ion adsorption at pH 2 (magnification power: $\times 50$ and $\times 250$) [37]. Reproduced from Ref. 36, with permission (License Number: 5356561306355) from Elsevier, 2022.

Cu(II), with removal efficiencies of over 70% and 40% for these species in five successive sorption-desorption cycles, respectively [38].

To test their ability to adsorb heavy metal cations, liquid-core capsules with a non-crosslinked alginate fluidic core surrounded by a gellan membrane were made in a single step [39]. At 25°C and pH 5.5, liquid-core gellan–alginate capsules made by dropping alginate solution containing magnesium cations into gellan solution were exceptionally effective at adsorbing lead cations (267 mg/Pb g dry alginate). These capsules, however, were quite weak and brittle, thus a magnesium cation-based external strengthening capsule was added. The membrane was subsequently thinned with the surfactant lecithin, resulting in capsules with greater adsorption properties (316 mg/g dry alginate vs. 267 mg/g dry alginate without lecithin), owing to the thinner membrane and improved mass transfer. The capsules' ability to adsorb other heavy metal cations, such as Cu(II), Cd(II), and Ni(II), was also investigated. The adsorption efficiencies were 219, 197, and 65 mg/g, respectively, and were related to the cation's alginate affinity. Heavy metal-sorbed capsules were regenerated by immersing them in a 1 M HNO₃ suspension for 24 h. Before getting damaged, capsules may go through three regeneration cycles [39].

The heavy metal ions Cd(II) and Cu(II) are used as model inorganic pollutants in aqueous solutions to evaluate the adsorption capability of the 3D network nanostructured calcium alginate (NN-CAlg) hydrogel. On the adsorption performances, the effects of dosage, pH, beginning concentration, contact time, and temperature are examined. The results of the tests demonstrate high removal efficiency, a fast adsorption rate, and a minimal amount of adsorbent. The NN-CAlg hydrogel's adsorption behavior is consistent with the Langmuir isotherm model and pseudo-second-order rate equation (PSORE). Thermodynamics and mechanism of adsorption are also investigated, with the results revealing a diffusion-controlled process and bidentate bridging (BB)/bidentate chelating coordination modes, respectively [40].

Copper(II) and cadmium(II) sorption from aqueous solution by calcium alginate and novel manufactured hybrid calcium alginate/pectate gel beads with varied alginate/pectate concentration ratios were evaluated using kinetic and equilibrium analyses [41]. Different methodologies were used to characterize the beads' physical and chemical properties (SEM, EDX, TGA). The ideal experimental pH conditions were chosen based on research on the acid-base characteristics of pectin and alginate in aqueous solution, as well as their ability to operate as Cu(II) and Cd(II) ion sequestering agents. The amount of calcium released during the sorption process was measured to figure out if there was an ion-exchange mechanism between the beads' calcium and metal ions in the solution. In batch mode, the sorption kinetics and metal sorption capacity of gel beads were examined. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to measure the concentrations of Cd(II), Cu(II), and Ca(II). The results revealed that the sorption process follows a PSORE in all of the tested systems and that the sorption rate increases as pectin concentration in gel beads increases. Both Langmuir and Freundlich isotherms models were

used to fit the equilibrium data. Copper(II) and cadmium(II) sorption yields were best in beads with a 2% alginate and 2% pectate combination. The main mechanism governing the sorption process is ion exchange, but additional mechanisms are also at work [41].

Alginate/polyethylenimine membranes are used to explore Hg(II) and Cu(II) sorption in single and binary systems [42]. To evaluate the metal sorption performance, batch studies are carried out. Metal-binding mechanisms are identified using FTIR and SEM-EDX studies. The PSORE fits the sorption kinetics better than the pseudo-first-order-equation (PFOE). For modeling the sorption in mono-component solutions, three isotherms are evaluated, Sips model providing the best simulation of experimental data. The competitive-Sips model fits sorption data in Hg-Cu binary solutions well, revealing that Hg competition significantly reduces Cu(II) uptake. Copper(II) uptake is minimal at low pH but rises with increasing pH up to 6 due to material deprotonation. Because of chloro-anion production, Hg(II) sorption behaves differently, slightly changing from pH 1 (q_e : 0.76 mmol/g) to pH 6 (q_e : 0.84 mmol/g). As a result, adjusting the pH allows Hg(II) to be separated from Cu(II) [42].

The modification of sodium alginate with thiosalicylic acid in the presence of calcium ions resulted in a novel adsorbent (TS-CAlg) [43]. The removal capability of Cu(II) and Cd(II) ions from aqueous solutions was examined using TS-CAlg. The adsorption impacts of batch and column parameters were systematically examined. The PSORE and Langmuir isotherm models fit the data from the biosorption results well. The highest biosorption capacities of TS-Alg for Cu(II) ions were found to be 426.9 and 592.9 mg/g for Cd(II) ions. The saturation points of TS-CAlg in the column system was 180 and 150 min for Cu(II) and Cd(II) ions, respectively. Finally, TS-CAlg has demonstrated outstanding efficiency in the removal of heavy metal ions using a smart biosorption approach, with advantages such as quick kinetics and large biosorption capacities [43].

To reduce the elevated load of toxic pollutants below the regulatory limits, real electroplating wastewater containing 51,190 mg/L of free cyanide (CNf), 4,899 mg/L of Ni, and 1,904 mg/L of Cu was treated with calcium alginate hydrogel beads, pure or impregnated with biodegraded grape marc (EBGM) or activated carbon [44]. The impacts of increasing the amount of adsorbent as well as the impact of two consecutive adsorption cycles on pollutant removal efficiency were assessed. In terms of raw wastewater, the most favorable sorption conditions on calcium alginate hydrogel beads resulted in removal percentages of 85.02% for CNf and 93.40%–98.21% for heavy metals. During the first 30 min of contact time, each pollutant's adsorption capacity on calcium alginate hydrogel beads was significantly increased, but after reaching equilibrium, the following sorption capacities were obtained: 1,177; 107.3; 39.5 and 1.52 mg/g for CNf, Ni, Cu, and Zn, respectively. The kinetic adsorption of contaminants onto the calcium alginate hydrogel beads was modified to various kinetic models, with the PSORE agreeing with the kinetic data. In the adsorption process, information about intraparticle diffusion pathways was also interpreted [44].

For the benefit of a cleaner environment, zero-waste industrial operations have recently been targeted. As a result, industrial waste is recycled and reused in self-manufacturing processes, as well as used in other industries and applications [45]. Steel industrial waste material, such as iron oxide nanoparticles (IONPs), was used to extract heavy metals like lead, cadmium, and copper from water in this study. To make IONPs-Alg nanocomposite, iron oxide waste was ground into nanoparticles (IONPs) and then incorporated into alginate (Fig. 4). FTIR, SEM, TEM, TGA, and XRD were used to verify the nanocomposite structure. After 30 min, the equilibrium sorption was established, with maximal capacities of 564, 158, and 102.2 mg/g for Pb(II), Cu(II), and Cd(II), respectively. The kinetic behavior was evaluated using the PFOE, PSOE, Elovich, intraparticle diffusion, and Bangham's kinetic models. The adsorption kinetic analysis found that PFOE was the best model for describing the adsorption of copper and lead ions onto IONPs-Alg nanocomposite, while PSORE was the best model for describing the adsorption of copper and lead ions onto IONPs-Alg nanocomposite. Five isotherm models were used to examine adsorption characteristics. The analyzed heavy metal ions adsorption behaviors were shown to follow the Freundlich isotherm model, confirming surface heterogeneity and an exponential distribution of active sites. The IONPs-Alg nanocomposite was also found to be an excellent nano-adsorbent for removing Pb(II), Cu(II), and Cd(II), respectively from wastewater samples [45].

Based on the commercial valorization of two plentiful waste biomass, *Padina boergeresii brown* alga and *Anadara uropigimelana* bivalve shells, a novel eco-friendly urea calcium alginate xerogel beads chemically functionalized with Congo red dye (U-Alg-CR_{1.43}) was manufactured sources [46]. FT-TR, BET surface area, TGA, SEM, and EDX studies were used to characterize the synthesized sorbent. The ability of the as-prepared adsorbent to trap Cu(II) metal ions sequentially was studied using a variety of operational parameters. The effects of sorbent dosages ranging from 0.5 to 5 g/L were investigated. Under an optimal pH value (i.e., pH = 6.5), sorption isotherms, uptake kinetics, and thermodynamic studies were also examined as prerequisite tools for a credible grasp of the adsorption mechanism. The isotherm profile of U-CAB-CR_{1.43} was found to fit the Langmuir equation, with a maximal sorption capacity of 6.94 mmol/g (441 mg/g). The PSORE was used to precisely fit the kinetic profile. The endothermic nature of the sorption process was highlighted by the thermodynamic function parameters. The wasted sorbent has been significantly boosted to be employed for up to four subsequent sorption/desorption cycles after a successful desorption scenario utilizing 0.5 mol/L of HCl [46].

The sorption of Cu(II) ions from artificial electroplating wastes was investigated using alginate beads adsorbent of mixed culture microalgae *Chlorella vulgaris*, *Chlorococcum* sp., and *Scenedesmus obliquus* in batch culture to determine the highest efficiency of Cu(II) adsorption. Adsorbent beads are manufactured by mixing 0.5 g (dead biomass)/g Na-alginate polymer. Cu(II) ions interacted with the adsorbent beads of these microalgae in the pH range of 4–6 and a contact time of 0–180 min. Copper(II) adsorption efficiency of 92% was achieved with an initial waste concentration of 25 mg/L and a pH of 4, 120 min of contact time, and a

temperature of 25°C. This study's sorption process is based on the Langmuir Isotherm, which has an R^2 value of 0.9991. It has been demonstrated that adsorbent beads of mixed culture microalgae may be utilized to manage Cu(II) pollution in the environment in an environmentally acceptable manner [47].

The sodium alginate-based hydrogel composite bead was fabricated from cationic hectorite clay and anionic sodium alginate using a simple ionic gelation process and freeze-drying, and the adsorption capabilities were determined by removing copper ions from aqueous solutions [48]. The results revealed that the adsorption process followed the Freundlich isotherm model, with a maximum sorption capacity of 160.28 mg/g at 45°C for initial concentrations ranging from 10 to 700 mg/L. PSOE fits the adsorption kinetics data well. The adsorption of Cu(II) ions was due to the porous nature of the composite. However, pH has the potential to improve adsorption [48].

Hydrogel beads were created to remove Au(III) ions from a scrap solid-state detector selectively [49]. Graphene oxide impregnation in a calcium alginate matrix (Gra-Alg) was used to prepare the adsorbent beads using the sol-gel process. Aqua regia was used to dissolve a scrap solid-state detector. Traditional chemical separation was used to recover Cu from the solution, whereas Gra-Alg hydrogel beads were used to selectively isolate Au(III) from the supernatant solution. The hydrogel beads' maximal adsorption capacity was found to be 81.87 mg/g. The sorption capacity of the hydrogel beads is significantly dependent on the pH of the solution, with over 95% Au uptake recorded at pH ranges 2–4. The gold sorption equilibrium contact time on the hydrogel beads was 22 h. According to the isotherm analysis, the system follows the Langmuir isotherm model, with a maximum sorption capacity (q_{max}) of 81.87 mg/g. The experimental data fitted well with the PSORE [49].

Alginate beads were used to increase the retention of cadmium ions from an aqueous medium [50]. There were two drying processes used: air drying and freeze-drying. Different techniques (i.e., SEM, BET, FTIR, TGA/DTG) were used to characterize the beads' physical and chemical properties. The freeze-dried beads (Alg-FD) have a smoother surface than the air-dried beads (Alg-AD), and they have almost maintained their original size, according to microscopic studies. The specific surface areas of Alg-AD and Alg-FD were discovered to be 0.039 m²/g and 56.83 m²/g, respectively. To better understand the adsorption process, researchers looked at the effects of pH and adsorbent dosage, as well as kinetic, equilibrium, and thermodynamic investigations. The kinetic sorption process follows the non-linear fitting of the Avrami fractional kinetic equation, and the sorption rate reduces as the pH of the medium is decreased. For Alg-AD, the Langmuir non-linear model fit the data well, while for Alg-FD, both Langmuir and Freundlich equations were used to describe the equilibrium data. Alg-FD absorbed more than Alg-AD, with maximal adsorption capacities of 60.98 mg/g for Alg-AD and 83.06 mg/g for Alg-FD, respectively. Furthermore, the calculated thermodynamic parameters ΔG° , ΔH° , and ΔS° , indicated that Cd(II) adsorption onto alginate beads is an endothermic, spontaneous, and physical adsorption process [50].

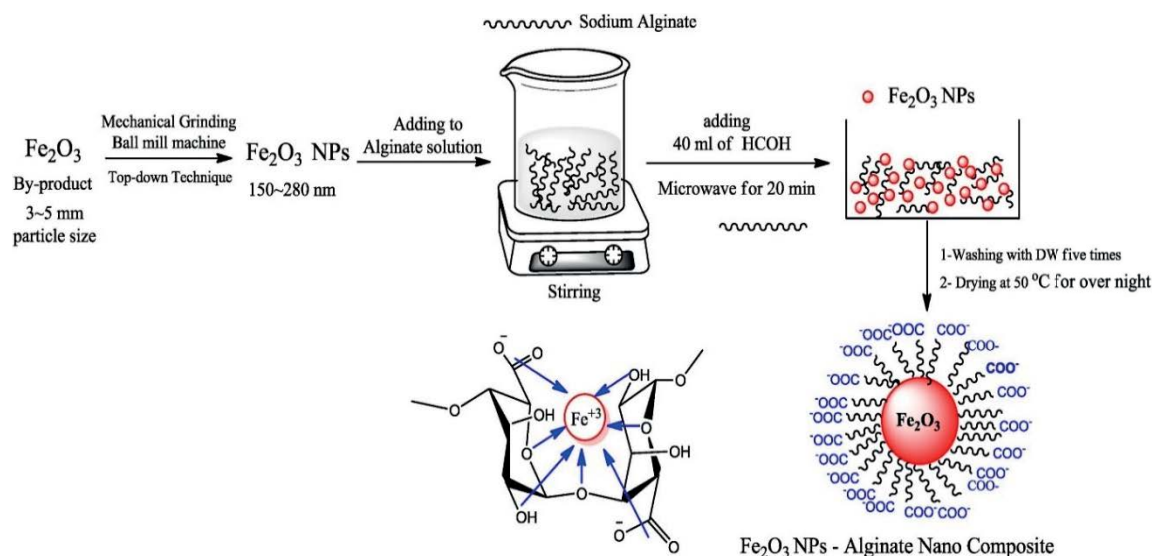


Fig. 4. Schematic diagram for the preparation of IONPs-Alg nanocomposite [45]. Reproduced from Ref. 43, with permission (License Number 5356590071553) from Elsevier, 2022.

Adsorbent material (AlgOx–TSC) based on alginate (Alg) chemically modified with thiosemicarbazide (TSC) has been created and evaluated to remove Pb(II) and Cd(II) ions from aqueous solutions [51]. The synthesis was carried out by regulating the following steps: (i) alginate partial oxidation in NaO₄ to obtain AlgOx, (ii) reacting AlgOx with TSC in NaBH₄ at 40°C–45°C. The produced AlgOx–TSC is a promising material capable of removing high concentrations of heavy metal ions such as Pb(II) (up to 950 mg/g at pH 3) and Cd(II) (up to 300 mg/g at pH 7) in aqueous solutions [51].

Because of the unpredictable contamination levels caused by scattered rainfall, stormwater runoff from airports creates significant Cd(II) pollution that exceeds the maximum allowed level and is difficult to remove [52]. A novel reactive filtering column has been created to overcome this and remove cadmium from runoff. The surface of an alginate bead was successfully implanted with sulfur functionalized polymer particles resulting in the formation of PS-Alg adsorbent, simulating a true stormwater treatment filtration column [52]. The PS-Alg has a batch sorption capacity of 22.3 mg/g and a continuous flow sorption capacity of 877 g/g for Cd(II) ions. In addition, the novel sorption material removed half of the Cd(II) ions in 6 min with a Langmuir sorption affinity of 31 L/mg. The reactive column exhibits 100% uptake of cadmium from a contaminated flow in a breakthrough test, which lasted 2 h until reaching the breakthrough point. The column's reusability was also confirmed by regeneration testing [52].

Alginate beads have been researched for their ability to adsorb Cd(II) ions from dilute aqueous solutions. The tests were carried out at a constant temperature of 25°C and a pH of 5.0. Over a wide cadmium concentration range of 0.3–3 mmol/L [53]. The equilibrium constants were discovered to be dependent on the alginate content in the beads, and the Langmuir equation was shown to accurately reflect experimental results. With increasing alginate content in

the beads, the maximum sorption capacity of Cd(II) ions was shown to decrease. The effective diffusivity (*D_e*) of the cadmium compounds was also calculated. The research was conducted using two methods: a shrinking core model (SCM) and a newly created conductometric approach. For calculating the effective diffusivity of Cd(II) in alginate sorbents, the conductometric method proved to be simple and effective. The alginate content in the beads affected the *D_e* values produced by the two procedures. In contrast to the conductometric method, the SCM method produced *D_e* values that increased with increasing alginate levels in the beads and were higher than the Cd(II) molecular diffusivity, which was incongruous with the mechanism of diffusion in porous carriers. As a result, the conductometric approach can be thought of as a more trustworthy method than the SCM method. Furthermore, the diffusion retardation coefficients in alginate beads were computed. Increased biopolymer content in the beads slowed Cd(II) diffusion in the beads because computed retardation factors decreased as alginate content in the beads increased [53].

Within the development of an effective adsorbent for heavy metal ions, organic-inorganic biohybrid composite adsorbent based on nanosized silica-titania modified with alginate was created [54]. Effect of Cu(II), Zn(II), Cd(II), and Pb(II) metal species, concentrations, pH, and temperature on adsorption onto titania-coated silica (ST20) or modified by sodium alginate (ST20-ALG) were investigated. Langmuir and Freundlich adsorption models, as well as kinetic models such as PFORE, PSORE, intraparticle kinetic model, and Elovich, were used to examine the equilibrium and kinetic data of metal ions adsorption. For all metal ions examined, the maximum sorption capacities reported for the ST20-ALG composite were higher than the original ST20, with values of 22.44 mg/g for Cu(II), 19.95 mg/g for Zn(II), 18.85 mg/g for Cd(II), and 32.49 mg/g for Pb(II) [54].

In alginate capsules, tetraalkylphosphonium dicyanamide was immobilized. This material was put through its paces when it came to adsorbing Cd(II) from HCl solutions. Metal sorption is mediated by ion exchange between Cd(II) ions and two dicyanamide groups. The concentrations of HCl and chloride ions did not affect the adsorption process. The Crank's equation (resistance to intraparticle diffusion) and the PSORE both accurately capture the uptake kinetics (chemical reaction rate) [55].

Two approaches have been used to immobilize Cyanex 301 and Cyanex 302 in alginate capsules: the matrix-type process immobilizes the extractant as homogeneous-dispersed vesicles, and the mononuclear mode encapsulates the extractant drop in an alginate layer. As a function of acid concentration and extractant, the effect of HCl concentration on Cd(II) removal is examined. The Langmuir model is used to fit the sorption isotherms; maximal sorption capacities in 0.1 M HCl approach 42 mg/g. Resistance to intraparticle diffusion regulates uptake kinetics. Cadmium is removed from solutions containing 1 M HNO₃ or 1 M thiourea/1 M HCl [56].

The sorption of Cd(II) and Pb(II) from aqueous solutions by CALg in batch systems was examined. The sorption capacities of CALg in each solution at different temperatures, as well as the kinetic and thermodynamic characteristics, were investigated. For both metals, the rate of sorption was rapid in the first 10 min. and reached a peak in 50 min. When comparing kinetic parameters for Cd(II) and Pb(II) sorption, it was discovered that the PSORE best describes these data; when comparing kinetic parameters for Cd(II) and Pb(II) sorption, a higher kinetic rate for Pb was observed, indicating that the interaction between Pb(II) cations and alginate beads was faster than for Cd(II). Isotherm data were also fitted to several models given in the literature, and it was discovered that the Langmuir–Freundlich (L-F) and Dubinin–Radushkevich (D-R) models accurately described the isotherms in all situations. At 25°C, CALg had a Cd(II) sorption capacity of 27.4 mg/g and a Pb(II) sorption capacity of 150.4 mg/g. As the temperature rises, the absorption capacity of Cd(II) and Pb(II) increases. The adsorption was spontaneous and endothermic, according to the thermodynamic characteristics. It was also shown that pH has a significant impact on CALg's ability to adsorb these metals, as more were eliminated at pH levels between 6 and 7 [57].

The grafting of urea and biuret on the backbone of alginate (verified by FTIR spectrometry analysis) boosts the biopolymer's sorption effectiveness for Cd(II), Cu(II), and Pb(II) recovery from moderate acidic solutions (pH in the range 4.5–5.5) by 53%–84%. The Langmuir and Sips equations successfully explain sorption isotherms, with maximal sorption capacities of 3.7 mmol Cd/g, 4.7 mmol Cu/g, and 4.8 mmol Pb/g for alginate-urea beads. The electronic properties (softness) and configuration of hydrated ions, as well as the hard and soft acid-bases rules properties of the ligands present on the sorbent, are all related to the sorbent's affinity for metal ions. Diffusion features are important in controlling uptake kinetic profiles, but the PSORE also allows for a fair fit of observed sorption kinetics. The sorbents in multi-component solutions have a stronger affinity for Pb(II) than the other two divalent cations [58].

Based on sodium alginate, calcium dihydrogen phosphate, and sodium hydrogen carbonate, phosphate-embedded calcium alginate beads were successfully produced. Pb(II) and Cd(II) sorption require pH levels of 4.0 and 5.5, respectively. Pb(II) and Cd(II) initial concentrations were 200 and 25 mg/L, respectively, with removal efficiencies of 94.2% and 80%. The heavy metal ions contacted the beads first because of their huge surface area, interacted with OH⁻, and then precipitated with phosphate radical, as demonstrated by FTIR and XRD. With R^2 values of 0.9957 and 0.988 the sorption of Pb(II) and Cd(II), respectively, is fitted to the Langmuir isotherm model. Pb(II) and Cd(II) had sorption capacities of 263.16 and 82.64 mg/g, respectively. These findings suggested that phosphate-embedded calcium alginate beads might be utilized to treat Pb(II)/Cd(II)-containing wastewater and that the synthesized beads could also be used as a type of soil ameliorant for heavy metal polluted paddy soil rehabilitation [59].

The use of sunflower waste carbon calcium alginate beads (SWC-CAB) for Cd(II) removal from wastewater in continuous flow fixed bed columns was described by Jain et al. [60]. The studies were carried out as a function of bed height, flow rate, and initial Cd(II) concentration. At 30 cm bed height, 1.0 mL/min flow rate, and 10 mg/L initial Cd(II) concentration, the maximum biosorption capacity (23.6 mg/g) was achieved. At 50% breakthrough time, the Bohart–Adams model constants (N_0 and K) were 7.7 mg/L and 1,104 L/mg h, respectively, with a 0.999 R^2 value. For Cd(II), the column regeneration efficiency after the third cycle was 58.6% [60].

A novel biomaterial, AlgS (sodium alginate functionalized with cysteine), has been produced, described, and tested to remove Pb(II) from aqueous media. AlgS ($q_{\max} = 770$ mg/g) has a maximum Pb(II)-sorption capacity that is nearly two to nine times higher than other alginate materials described in the literature. The chemical alteration of alginate at the oxidation and aminofication stages has been studied using techniques such as TGA/DSC, SEM/EDS, BET, FTIR, UV–Vis, XRD, and ¹³C solid state-NMR. A UV band at 348 nm revealed the production of the imine intermediate (C=N) after 24 h of reaction. AlgS has typical IR bands at 2,970; 955; 949 and 1,253 cm⁻¹, which correspond to CH, SPb, SH, and CN stretching vibrations, respectively. Peaks at 33–38 ppm and 55–60 ppm in the ¹³C solid state-NMR spectra of AlgS are associated with (HS-CH₂-) of cysteine and (CN), respectively. Pb(II) sorption has negative ΔH° and ΔG° values, indicating that it is an exothermic process that occurs spontaneously. Finally, it was discovered that the presence of cationic (Na⁺, Mg²⁺, and Al³⁺) and anionic (Cl⁻, NO₃⁻) co-ions had a considerable impact on Pb(II) sorption on AlgS [61].

An interesting application of alginate beads is to create CALg beads that could adsorb lead ions at stomach pH so that they might be used in gastric lavage in the event of lead poisoning [62]. Both dry and hydrated beads were subjected to swelling tests in simulated stomach fluid (SGF). At lead concentrations ranging from 50 to 200 mg/L, the sorption kinetics were investigated. The amount of calcium released during the sorption process was studied. The dry beads' swelling rate grew significantly with time, reaching an equilibrium of 736% after 240 min; the hydrated beads'

equilibrium swelling reached 139% after 180 min. Lead(II) adsorption in SGF by dry beads increased as time and initial lead concentration rose. The adsorption kinetics of Pb ions by hydrated alginate beads revealed that for all concentrations, fast binding of Pb ions to the sorbent occurred during the first 15 min, followed by a steady increase until equilibrium was reached after 90 min. The adsorption capacity of Pb ions increased as the storage duration and weight in water at 4°C increased. The amount of Ca²⁺ released by the beads rose at a faster rate as the amount of Pb ions increased [62].

Table 1 shows the maximum adsorption performances onto functionalized alginate-based sorbents with a series of values found in the literature (together with the best-operating conditions reported by respective authors). This is a useful criterion for roughly evaluating the potential of these materials. The thiosalicylic acid-modified alginate sorbents have the highest adsorption capacity for Cu(II) and Cd(II) ions; although alginate–chitosan hybrid gel beads showed the lowest adsorption capacity, they have the best kinetic behavior. It is noteworthy that the Sodium alginate with iron oxide waste material from steel industry sorbents has the highest adsorption capacity (5,000 mg/g) for Pb(II) ions. The high sorption capacity of the various alginate-based adsorbents towards Cu(II), Cd(II), and Pb(II) ions reveals that adsorbents could be promising for practical application in heavy metal ions removal from wastewater.

4. Alginate-based composites

By reusing materials already extracted in a new production cycle, the recovery of these metals in secondary sources is of significant environmental and economic relevance. Barcelos da Costa et al. [72] tested if sericin/alginate particles crosslinked with poly(vinyl alcohol) (ALPVA) might be used for batch ytterbium adsorption. Three ytterbium initial concentrations (0.0005, 0.0011, and 0.0015 mol/L) were used in the kinetic investigation. After around 300 min, kinetic equilibrium was established. The ytterbium adsorption was explained by PFO rate equation and external diffusion, according to the kinetics modeling of the experimental data. Several eluents were used to test ytterbium desorption. Nitric acid, at a concentration of 0.3 mol/L, had the highest recovery efficiency of these eluents. Adsorption kinetics with the regenerated particles, on the other hand, revealed an equilibrium time of 120 min with total calcium release. The uptake of ytterbium ions and calcium release is thought to be mediated by an ion exchange mechanism between carboxyl and hydroxyl groups and ytterbium, according to the characterization of ALPVA particles before and after the adsorption process. The usage of SAPVA particles showed a lot of promise in terms of ytterbium recovery from wastewater [72].

Nanosized materials can remove pollutants and biological contaminants efficiently in the field of environmental remediation [73]. The preparation of an alginate caged magnetic graphene oxide bio-polymeric nanocomposite bead (Alg-MGO) was done. The magnetic solid-phase extraction (MSPE) method is used for determining Cu(II) and Pb(II) in urine, saliva, and river water samples [74]. The linear concentration range obtained was 0.33–25.00 g/L with an

acceptable coefficient of determination ($R^2 = 0.99$) and a low limit of detection (LOD = 0.21–0.71 g/L, $n = 3$). With the help of standard reference material. The elimination of metal ions was investigated using isotherm models at high concentrations (1–200 mg/L). Because of the high coefficient of determination (R^2) and suitable adsorption capacities of 96.13 and 103.09 mg/g for Cu(II) and Pb(II), respectively, the Langmuir isotherm is well matched to the data. For the uptake of selected metal ions from an aqueous solution, a thermodynamic model is proposed with a spontaneous process, endothermic nature, and physical sorption mechanism [74].

Scientists have been particularly interested in metal-organic frameworks (MOFs) because of their superior adsorption properties. The difficulty in extracting MOFs from adsorbed metals after usage, however, has limited their utilization. The application of a zeolitic imidazole-based MOF for Pb(II) sorption is investigated [75]. Sodium alginate and ZIF-8 were used to create a new adsorbent with ZIF-8/calcium alginate microparticles. The effects of the initial Pb(II) concentration, reaction time, pH, and reaction temperature on the reaction process were explored, as well as the performance of the ZIF-8@CALg microparticles in adsorbing Pb(II) from a Pb(II) solution. After 120 min, ZIF-8@CALg microparticles had a maximum adsorption capacity of 1,321.21 mg/g at pH 5, and the adsorption process fit the Langmuir isotherm model ($R^2 = 0.9856$), and the PSORE ($R^2 = 0.9999$), according to the findings. These findings revealed that Pb(II) adsorption is an endothermic process. Even after five cycles, the removal effectiveness of Pb(II) was better than 80% in the regeneration experiment with ZIF-8@CALg [75].

The modification of alginate by free radical polymerization of 2-acrylamidoglycolic acid utilizing a potassium peroxydiphosphate/silver nitrate redox system in an inert atmosphere is described by Yadav et al. [34]. Variations in reaction variables such as 2-acrylamidoglycolic acid concentration (2.01–7.31 mol/L), potassium peroxydiphosphate concentration (0.41–2.01 mol/L), silver nitrate concentration (1.21–4.41 mol/L), sulphuric acid concentration (1.01–8.10 mol/L), and alginate concentration (0.4–1.8 g/L), as well as time duration (60–180 min) were investigated. In comparison to the parent polymer, water swelling capacity, metal ion sorption, flocculation, and resistance to biodegradability experiments of synthesized graft copolymer were conducted [34]. The thermal data show that the synthesized graft copolymer is thermally more stable than pure alginate. The synthesized graft copolymer, that is, alginate-g-2-acrylamidoglycolic acid shows better results for swelling, and flocculating properties in comparison to alginate, this could be interpreted as graft copolymer shows the enhancement in these properties. The spectroscopic data confirm that the grafting of 2-acrylamidoglycolic acid might have taken place in the hydroxyl group, which is supported by a tentative mechanism suggested for grafting. The thermal analysis data show that graft copolymer, a hybrid material in which properties of monomer are added by grafting, could be exploited very well industrially [34].

Prussian blue graphene oxide alginate (PB-GO-Alg) composite in beads form was prepared using a simple hydrothermal procedure followed by a displacement

Table 1
Copper(II), cadmium(II), and lead(II) adsorption performances onto functionalized alginate-based sorbents

Metal ion	Sorbent	pH ₀	Equilibrium time (min)	$q_{m,L}$ (mg/g)	b_L (L/g)	References
Copper(II)	Alginate/polyethylenimine membranes	5	360	34.29	40.8 ± 12.1	[42]
	Iron oxide particles with alginate	5.4	60	46.15	44.30	[17]
	Thiosalicylic acid modified alginate	5.5	30	426.9 ± 5.8	0.202	[43]
	Alginate	5	120	112.1	0.03	[63]
	Alginate-chitosan	5	120	121.0	0.01	[63]
	Sodium alginate with iron oxide waste material from the steel industry	5	30	769.23	1.0718	[45]
	Activated bentonite-alginate composite	5	600	17.30	0.104	[64]
	Alginate-modified spinel ferrite	6	50	63.9	0.031	[65]
	Porous calcium alginate/graphene oxide composite	4	40	180.27	0.473	[66]
	Polyaniline-alginate microsphere	5	50	67.95	2.8	[67]
	Alginate–chitosan hybrid gel beads	3.5	10	8.39	4.064	[68]
	Thiosalicylic acid modified alginate	7.5	30	592.9 ± 1.4	0.406	[43]
	Cadmium(II)	Alginate	5	120	144.34	0.04
Alginate-chitosan		5	120	113.92	0.01	[63]
Sodium alginate with iron oxide waste material from steel industry		6	30	1,000	8.953	[45]
Porous calcium alginate/graphene oxide composite		4	40	96.69	0.415	[66]
Biochar-alginate composite		6.0	60	9.73	–	[69]
Alginate–chitosan hybrid gel beads		3.5	10	6.63	27.76	[68]
Sodium alginate with iron oxide waste material from steel industry		6	30	5,000	4.522	[45]
Lead(II)	Activated bentonite-alginate composite	5	600	107.52	0.653	[64]
	Alginate-modified spinel ferrite	6	50	96.9	0.043	[65]
	Porous calcium alginate/graphene oxide composite	4	40	366.83	0.493	[66]
	Biochar–alginate capsule	5	120	263.158	0.026	[70]
	Polyaniline-alginate microsphere	5	12	251.45	0.13	[67]
	Calcium alginate–xanthan gum hybrid bead composites	6	120	18.868	0.053	[71]

reaction for very efficient removal of Cs isotopes from aquatic environments [76]. The optimal bead composition was a 5% loading of PB (Prussian blue)-GO (Graphene Oxide) nanoparticles in a 4% Ca-alginate matrix. When GO is functionalized with PB, a zeolite-like inorganic material capable of exchanging K ions for Cs ions, it becomes a zeolite-like inorganic material. The hybrid beads showed outstanding removal effectiveness (>98%) for Cs isotopes from various aquatic habitats due to the combined impacts of GO, PB, and the host alginate matrix. The maximal sorption capacity of Cs was predicted to be 290.6 mg/g using the Langmuir model ($R^2 = 0.95$). The uptake followed the PSORE, according to kinetic analysis. The beads were successful for Cs removal at pH 5–7 (uptake >98%) and required a 6 h equilibrium time. The zeta potential values of the GO and PB-GO nanocomposites at varied pH were used to propose a mechanism of sorption [76].

Decontamination of dilute industrial effluents is a key challenge for reducing mining and metallurgical industries' environmental impact. An extractant impregnated resins (EIRs) have been manufactured as an alternative to

traditional approaches by immobilizing Cyanex 301 and Cyanex 302 in alginate capsules using two separate procedures (matrix-type immobilization vs. mononuclear encapsulation) [77]. Pb(II) sorption from acidic solutions has been tested on these materials. The maximal sorption capacities vary from 24 and 80 mg/g at pH 1 depending on the kind and loading of the extractant in the EIR, and the Langmuir equation fit the sorption isotherms well. The resistance to intraparticle diffusion-controlled uptake kinetics, though the Crank equation (intraparticle diffusion) and the PSORE both match uptake profiles equally well. Mononuclear capsules have a lower amount of extractant immobilized than matrix-type beads, resulting in poorer sorption capacities but slightly better mass transfer qualities. The advantages and disadvantages of the various systems are balanced in matrix-type capsules, making them more promising. metal ions were desorbed using 1 M HNO₃ solutions for desorption of Pb(II). However, when the extractants are re-used, the sorption effectiveness is reduced due to possible oxidation (conversion to oxidized forms more sensitive to pH) [77].

For the elimination of Pb(II), another adsorbent was created using iron oxide nanoparticles and *Agrobacterium fabrum* (SLA)731 strains encapsulated in calcium alginate [78]. The crude oil degrading strain was isolated from core samples from the Assam Oilfield in India and was shown to be highly lead tolerant, with resistance to lead of up to 2,900 mg/L. Various approaches were used to analyze chemically generated Fe₃O₄ magnetic nanoparticles (10–20 nm) made via co-precipitation. According to the Vibrating Sample Magnetometer (VSM), the saturation magnetization of synthesized MNPs was 46.6 emu/g, suggesting superparamagnetic nature, which will aid in the separation of the adsorbent following adsorption. The adsorption capability of a biosorbent produced by immobilizing biomass and MNPs in calcium alginate beads at 200 rpm and 37°C for lead removal was found to be highest at pH 5.5. The PSOE fit the kinetic data, and the adsorption rate constant (k_2) declined as initial concentrations increased. It was discovered that the initial adsorption rate (h , mg/g min) is kinetically controlled and a function of the initial Pb(II) concentration. After 60 min of adsorption, the IPD was discovered to be the rate-limiting step. The Langmuir isotherm fit the adsorption data well. The synthesized bio-maximal sorbent's adsorption capacity was determined to be 197.02 mg/g. The adsorption process appeared to be spontaneous and endothermic, according to thermodynamic studies. Even after being used for five consecutive cycles, Biosorbent exhibited good adsorption capacity without affecting adsorption efficiency [78].

The sorption capacity of heavy metal ions (Pb(II) and Cd(II)) by hydroxyapatite-alginate/gelatin (HA/Alg/Gel) nanocomposite was studied as a function of adsorbent dose, adsorbate concentrations, and contact time. PSORE was the best fit by the sorption kinetics, and the equilibrium followed the Langmuir isotherm model. The equilibrium elimination capacity of the HA/Alg composite was calculated using the Langmuir isotherm model to be 550 mg/g for Pb(II) and 361 mg/g for Cd(II). While the removal capacity of the HA/Alg/Gel composite was determined to be 616 and 388 mg/g for Pb(II) and Cd(II), respectively. In a binary metal ion system, the adsorbent's ability to remove a specific metal ion was hampered by the presence of another ion in the medium [79].

4.1. Biomass-modified alginate

Pb(II), Cd(II), and Hg(II) removal from aqueous solutions were investigated using waste biomass from *Bacillus cereus* immobilized in the sodium alginate and co-immobilized with activated carbon or bentonite into alginate gel [80]. The composite adsorbent made up of waste *B. cereus* biomass immobilized with activated carbon in alginate beads was found to be the most promising for heavy metal removal. Immobilization boosted the adsorbent's removal capacity as well as its mechanical strength. At pH 5.0, adsorbent dosage of 2 g/L, temperature of 25°C, and agitation speed of 120 rpm for 120 min, the maximum removal efficiency of 92.13% for Pb(II) ions was achieved [80].

The red algae *Jania rubens* were placed in a polyvinyl alcohol/calcium alginate (PVA/CaAlg) matrix to remove lead from aqueous solutions [81]. The uptake of Pb(II) was

fast and reached its equilibrium after 2 h. The optimum pH was 5, Langmuir and Freundlich models suit the data well. At 30°C and pH 5, the sorption capacity (q_e) of PVA/CAlg/*Jania rubens* matrix rose from 10.77 to 37.195 mg/g as the Pb(II) concentration increased from 24.86 to 98.75 mg/L. The maximal biosorption (q_m) and sorption capacity (q_e) were calculated to be 37.179, 0.32 and 71.43 mg/g, respectively. A PSORE of the adsorption process was found to be very accurate. Endothermic, spontaneous, and increasing in randomness, this reaction is endothermic and spontaneous. The functional groups OH, CN, CO, CONH, NH₂, SH, and COOH, which were all present on the matrix, were all heavily engaged in the adsorption process. The morphological alterations caused by Pb(II) adsorption on and inside the PVA/CAlg/*Jania rubens* matrix were shown by scanning electron microscopy data. the PVA/CAlg/*Jania rubens* biomass matrix regenerates efficiently for three cycles, indicating that it is a good matrix for Pb(II) removal and may be employed in continuous systems, according to the desorption investigation [81].

The impact of brown algae that was immobilized and the role of *Fucus vesiculosus* in heavy metal biosorption with alginate xerogels were investigated [82]. The three metals' kinetic uptakes and intraparticle diffusion rates were increased when they were immobilized. For Cd(II), the Langmuir maximum biosorption capacity increased double, tenfold for Pb(II), and half for Cu(II). The metals' affinity for biomass, according to this hypothesis, was as follows: Without alga, Cu > Pb > Cd, whereas with alga, Pb > Cu > Cd. Carboxyl groups were the major groups implicated in metal uptake, according to FTIR. According to the "egg-box" hypothesis, heavy metals from the solution displaced calcium in the gels. SEM examination revealed that the reconstructed gel matrix became more homogenous and ordered. *F. vesiculosus* immobilized in alginate xerogels is an effective adsorbent for Cd(II), Pb(II), and Cu(II) [82].

The potential utilization of immobilized microalgae (*Chlamydomonas reinhardtii*) in Ca-alginate to remove Hg(II), Cd(II), and Pb(II) ions from aqueous solutions was examined [83]. For 5 d, Ca-alginate beads containing immobilized microalgae were incubated at 22°C for homogeneous growth. The effects of pH, temperature, initial metal ion concentrations, and adsorbent doses on Hg(II), Cd(II), and Pb(II) ion adsorption were investigated. At pH 5.0 to 6.0, the adsorption of Hg(II), Cd(II), and Pb(II) ions on immobilized microalgae showed the highest values. The immobilized microalgae adsorption of these ions followed second-order kinetics, and equilibrium was reached in around 60 min. The adsorption capabilities of the immobilized microalgae were unaffected by temperature changes in the range of 5°C–40°C. For Hg(II), Cd(II), and Pb(II) ions, 2 M NaCl can be used to renew the immobilized-algal systems [83].

Another adsorbent containing alginate encapsulated with *Myriophyllum spicatum* (MsAlg) was tested for the removal of Pb(II) ions [84]. According to FTIR research, ion exchange and Pb(II) complexation with the carboxyl, carbonyl, and hydroxyl groups in MsAlg were found to be part of the Pb(II) ions sequestration mechanism. To gain a better understanding of the mechanics of Pb(II) binding on kinetic data removal of lead ions on three materials: *M. spicatum*, Ca-alginate, and MsAlg, three reactions and

one diffusion-based kinetic model were used. The adsorption capacity of *Myriophyllum spicatum* encapsulated with alginate (MsAlg) is higher than that of *M. spicatum*. With capacities ranging from 230 to 268.7 mg/g, the Redlich-Peterson and Langmuir isotherm models had the best fit to the experimental data among the six isotherms studied. Nitric acid has shown to be the most effective desorption agent of the several that have been tested [84].

A new complex of polyvinyl alcohol (PVA) and sodium alginate impregnated with sulfate-reducing bacteria (SRB) was successfully manufactured, and this flexible bio-composite was used to remove hazardous Pb(II) from aqueous solution [85]. After Pb(II) removal, the surface of immobilized SRB beads changed dramatically and became significantly smoother. The sorption data revealed that the pH of the solution was critical for the removal of Pb(II) ions. The sorption of Pb(II) increased as the initial concentration of Pb(II) ion rose, and the best temperature for Pb(II) removal is 35°C. With 50 mg/L of Pb(II) in the reactive system, the highest removal efficiency of Pb(II) was seen at 35°C and pH 8.0. PSORE and Langmuir models accurately represented the bio-removal kinetics of Pb(II) by immobilized SRB beads, with good kinetic fitting results and isotherms studies. Under ideal conditions, the maximum adsorption capacity was found to be 707.3 mg/g [85].

The adsorbents for the removal of Pb(II) ions from polluted water employing batch methods of extraction are nitric acid activated carbon derived from the seeds of the *Caryota urens* plant (ACSCU) and CALg beads doped with the active carbon (CALgBCU) [86]. The extraction conditions are tuned for maximal (89.0% for ACSCU and 96.0% for CALgBCU) removal of Pb(II) by adjusting various physicochemical factors such as pH, initial concentration of Pb(II), sorbent dosage, temperature, equilibration period, and presence of co-ions (II). The adsorption capabilities of ACSCU and CALgBCU, respectively, were found to be 42.9 and 86.9 mg/g. Even after five adsorbent regenerations, a significant proportion of Pb(II) is eliminated (at least 80%). The adsorption is endothermic and spontaneous. The PSORE accurately describes the kinetics of adsorption. The established methodology has been applied to wastewater samples obtained from diverse companies with great success [86].

It was reported that brown algae can be incorporated into biopolymer beads or foams for metal sorption. However, using these biomasses directly to make foams is a novel strategy. Two types of porous foams were generated by ionotropic gelation utilizing algal biomass (*Laminaria digitata*) or alginate (as a control) and used for Pb(II) sorption [87]. The foams (which were made as macroporous discs) were packed in filter holders (which mimicked a fixed-bed column) and the system was run in either a recirculation or a one-pass mode. The Langmuir equation accurately describes sorption isotherms, while the PSORE accurately describes both sorption and desorption kinetic profiles. Even after 9 cycles, the investigation of material regeneration reveals that the foams can be reused with minimal mass loss. In the one-pass mode, a slower flow rate resulted in a reduced saturation volume for alginate foams, while the effect of flow rate was less pronounced for algal biomass foams. According to competitive research, the foams prefer

Pb(II) to Cu(II), but they are unable to selectively remove Pb(II) from the binary solution [87].

In the absence and presence of Ca, the binary adsorption of Pb(II) and Cu(II) onto calcium alginate, algal biomass, and algal/glutaraldehyde-crosslinked polyethyleneimine (PEI) composite beads were investigated [88]. For predicting equilibrium data, different competing models were evaluated. In the Pb-Cu binary system, all sorbents have a strong preference for Pb(II) over Cu(II): the separation factors for alginate, algal biomass, and algal/PEI beads are 14.1, 9.1, and 3.6, respectively. As the sorption sites become saturated, kinetic investigations demonstrate the existence of an ion-exchange process between Pb(II) and Cu(II). For all sorbents, the competitive Sips model accurately predicts sorption data. Cu(II) sorption by algal beads was insignificant in the Pb-Cu-Ca system, but algal/PEI maintained a large Cu(II) sorption under these conditions [88].

The role of Pb(II) sequestration by immobilized bio-film-related extracellular alginate-based polymeric substances (EPS) of the marine bacterium *Pseudomonas aeruginosa* N6P6 was examined [89]. The authors discovered that immobilized biofilm-produced EPS contributes significantly to Pb(II) sequestration when compared to pristine alginate beads by comparing Pb(II) sequestration on immobilized living biomass and pristine alginate beads. To determine the optimal conditions for maximum Pb(II) removal by various adsorbents, the pH was varied from 3 to 8 and the initial Pb(II) concentration was varied from 100 to 600 mg/L. The EPS alginate beads had a considerably better Pb(II) biosorption capacity (416.67 mg/g) than alginate biomass beads (232.55 mg/g) and pristine alginate beads (120.48 mg/g). The optimum pH was 6. The adsorption isotherms, Langmuir, and Freundlich-type models were found to fit the experimental data well ($R^2 = 0.99$). Pb(II) adsorption (68.33%) and desorption (66.8%) from contaminated water were used to test the reusability of the EPS alginate adsorbent after three adsorption/desorption cycles [89].

In a continuous packed-bed column under dynamic conditions, the adsorption capabilities of alginate, chitosan, and immobilized *Spirulina platensis-maxima* cells were investigated [90]. Alginate and chitosan bead composition was improved. The influence of flow rate, column height, and initial metal ion concentration was examined under various operating conditions. Cu(II), Cd(II), and Pb(II) ions have the maximum adsorption capacity in alginate beads, with 3.4, 2.3, and 3.1 mmol/g per dry weight, respectively. The adsorption capacity of the alginate-*Spirulina* system was marginally reduced (3.1, 1.9, and 3 mmol/g). Cu(II), Cd(II), and Pb(II) adsorption by chitosan and chitosan-*Spirulina* beads are 0.8, 0.9, 0.7, and 1, 0.8, 0.6 mmol/g, respectively. The findings show that the beads can be reused for at least five sorption cycles [90].

4.2. Biochar-modified alginate

Water hyacinth (*Eichhornia crassipes*) biochar is an excellent adsorbent for the removal of some heavy metals and as a control for this extremely invasive species. The Cd(II) sorption kinetics of alginate encapsulated water hyacinth biochar (i.e., biochar-alginate capsule; BALgC)

produced at different temperatures and modified with ferric/ferrous sulfate to produce modified biochar-alginate capsule (MBAIgC) was investigated by Liu et al. [91]. At pH 6, and a solution temperature of 37°C, the greatest Cd(II) sorption occurred. Both the Langmuir ($R^2 = 0.876–0.99$) and Freundlich ($R^2 = 0.849–0.971$) equations fit the sorption equilibria for BAC and MBAC treatments. With maximal sorption capacities ranging from 24.2 to 45.8 mg Cd²⁺/g, Langmuir isotherms fit better than Freundlich isotherms. Larger K_L values indicate significant bonding of the BAC and MBAC sorbents to Cd(II), with K_L values in the MBAC treatments ranging from 31% to 178% higher than in the BAC treatments. Cd²⁺ sorption followed PFOE kinetics ($R^2 = 0.926$ to 0.991), with treatments with biochar produced at temperatures >500°C resulting in higher removal effectiveness [91].

Heavy metals were fixed in soils to lower their bioavailability during remediation of Magnetic porous biochar spheres and their functions in heavy metal *in-situ* sorption and removal from contaminated agricultural soil were investigated [92]. The magnetic biochar spheres were made by combining alginate and FeCl₃ in a one-step gelation process to produce an alginate-Fe(III) gel, which was then pyrolyzed. When the spheres were pyrolyzed at 300°C, the results of an ultraviolet-visible spectrophotometer, X-ray diffraction, and Fourier transform infrared spectrometer revealed the disintegration of alginate and the creation of Fe₃O₄ and FeCl₂ hydrate nanoparticles on the spheres. The spheres have a macro-porous structure, according to a scanning electron microscope image. The studied spheres were shown to have a high capacity for adsorption of Cr(VI) from an aqueous solution. The bioavailable and total Cd(II) concentrations were reduced by the spheres from 1.55–0.08 to 0.32–0.04 mg/kg and 2.81–0.02 to 1.39–0.06 mg/kg, respectively. Furthermore, the spheres reduced bioavailable and total As(V) concentrations, respectively, from 1.26–0.003 to 0.85–0.01 mg/kg and 60.23–0.39 to 27.34–0.94 mg/kg. Water was then added to the soil, which caused the spheres to leave the soil and float on the surface of the soil/water mixture. As a result, utilizing magnets, the magnetic biochar spheres can be considerably easier to extract from the soil [92].

Because of their high specific surface area and large accessible pores, carbon aerogels are gaining popularity as adsorbents. The manufacture of a magnetic carbon aerogel (MCAIg) employing sodium alginate (NaAlg) as the main carbon source, gelatin (G) as a cross-linking agent, and secondary carbon source, and Fe₃O₄ nanoparticles as the magnetic component was described by Li et al. [93]. A Fe₃O₄/SAIg/G hydrogel precursor was converted into the MCAIg using a simple pyrolysis process at 550°C under N₂. The magnetic carbon aerogel produced had a large specific surface area (145.7 m²/g), a hierarchically porous structure, and an abundance of surface hydroxyl (–OH) and carboxyl (–COOH) groups, resulting in excellent adsorption capabilities for Cd(II) ions (adsorption capacity reached 143.88 mg/g). The mechanism of Cd(II) adsorption by the MCAIg was examined, and the findings suggested that the MCAIg removed Cd(II) ions from water through both electrostatic adsorption and complexation. The MCAIg could be easily isolated and retrieved from water because they contained Fe₃O₄ nanoparticles [93].

The efficacy of powdered activated carbon impregnated alginate beads (AlgAC) in removing Cd(II) from the water was investigated. Cadmium adsorption by AlgAC was studied as a function of contact time (1h–11d), initial pH (4–7), and initial Cd(II) concentrations (10–600 mg/L) [94]. AlgAC had a sorption capacity of 149.32. The PSORE with correlation coefficients of $R^2 > 0.994$ accurately represented the sorption kinetics. Cadmium sorption capacity increased from 41.76 to 56.09 mg/g when the pH was raised from 4 to 7 [94].

By dropping a combination solution of biochar (BC) and calcium chloride (CaCl₂) into an alginate (Alg) solution and altering the mass ratio of BC to Alg, biochar–alginate capsule (BAIgC) was successfully manufactured (Fig. 5) [70]. The elimination of Pb(II) from an aqueous solution was used to study the BAIgC's adsorption properties. At a pH of 5.0 and a contact time of 120 min, the maximum adsorption of Pb(II) was evaluated well. The highest sorption capacity of Pb(II) by BAIgC's (BC:Alg = 8:1) was 263.158 mg/g, which is substantially greater than the capacity of other adsorbents, according to the Langmuir isotherm, which was a better fit than the Freundlich isotherm. The PSORE ($R^2 = 0.997$) was properly followed by the sorption. After the Pb(II) adsorption process, the BAIgC's was easily recovered and highly recoverable (90%–95%) using an HNO₃ solution. Even after being recycled 10 times (repeated adsorption/desorption), the recovered BAIgC adsorption efficiency remained around 70% of the initial adsorption capacity [70].

For the elimination of aqueous Cd(II), a new adsorbent was created by encasing ball-milled biochar in Ca-alginate beads [95]. Cadmium(II) adsorption characteristics of ball-milled biochar (BMB), Ca-alginate (CAIg), and Ca-alginate entrapped ball-milled biochar were compared in batch adsorption studies (CAIg-BMB). The sorption ability of all of the adsorbents tested was outstanding. With Langmuir isotherm modeling, the maximal Cd(II) adsorption capacity was determined to be 251.8 mg/g for CAIg, 227.1 mg/g for CAIg-BMB, and 40.0 mg/g for BMB. The findings show that trapping ball-milled biochar in Ca-alginate is a low-cost, high-effective method for removing aqueous Cd(II) [95].

4.3. Chitosan modified alginate

The heavy metal ions Cd(II) and Cu(II) were removed from aqueous solutions using chitosan immobilized in alginate (Alg-Chs) [63]. The research has revealed that the pH of the solution does not affect the adsorption efficacy of either Cd(II) or Cu(II) ions in the Alg-Chs sorbent, which expands its application possibilities. The Sips model was used to determine the maximum sorption capacity of the tested sorbent. Based on the ARE value, it has been demonstrated to be the best fit for the experimental data. The predicted sorption capacities for Cd(II) and Cu(II) were 527.3 and 207.0 mg/g, respectively [63].

Copper(II) ions were removed from aqueous solutions using fixed-bed columns packed with alginate-chitosan (Alg-Ch) or alginate-chitosan sulfate (Alg-ChS) hydrogel beads at a pH of 5.0 [96]. The amount of Cu removed by the column at the breakpoint and exhaustion points is affected by the initial Cu(II) concentration, flow rate, pH, and column height. The pH of the solution at the exit of the column

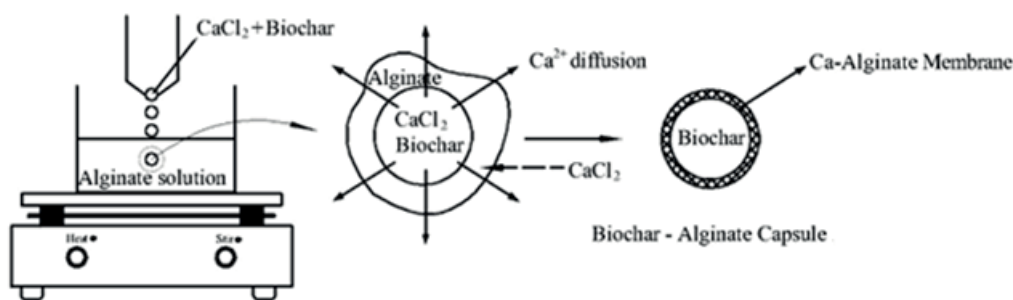


Fig. 5. Schematic diagram for the preparation of biochar-alginate capsule [70]. Reproduced from Ref. 71, with permission (License Number 5356170454284) from Elsevier, 2022.

was originally greater than that at the entry, but it gradually declined. Proton transfer from the aqueous solution to the amino and COO groups of the hydrogel was blamed for the pH increase. It is discussed how operating conditions affect the mass transfer zone (MTZ) and the length of the unused bed (HLUB). The MTZ was established and the column ran efficiently at the lower flow rate and Cu(II) concentration employed; raising column height gives the MTZ a greater chance to fully grow. A non-linear regression analysis was used to fit experimental data to the fixed-bed Thomas model, and a strong correlation between experimental and Thomas model curves was obtained [96].

Binary (chitosan-Cu(II), CCu) and ternary (chitosan-alginate-Cu(II), CALgCu) composite materials of various compositions were synthesized: CCu (1:1), CALgCu1 (1:1:1), CALgCu2 (1:2:1), and CALgCu3 (1:3:1). (2:1:1) [97]. The materials' characterization validated the polymer-based composites' successful synthesis, as well as their varied physicochemical and adsorption capabilities. The removal of the sulfate anion (sodium sulfate) from the aqueous solution was achieved using CALgCu1 at pH 6.8 and 295 K, with monolayer adsorption capacity values of 288.1 and 371.4 mg/g, respectively, with the Sips isotherm model providing the best fit for the adsorption data. According to the sorption study on three types of groundwater samples (wells 1, 2, and 3) with variable sulfate concentration and matrix composition in the presence of composite materials, in general, the binary composite material (CCu) had lower sorption and removal effectiveness than the ternary composite materials in all groundwater samples (CALgCu) [97].

4.4. Clay/minerals modified alginate

The removal of Cu(II) and Pb(II) ions using activated bentonite-alginate (ABn-Alg) composite beads can be easily separated and recovered after the adsorption reaction [64]. Fig. 6 shows a schematic representation of acid activation of bentonite and preparation of activated bentonite alginate composite beads. The type IV isotherm for nitrogen adsorption-desorption was established for the materials, with H3 hysteresis loops confirming the presence of mesopores with slit-shaped pores. Batch studies revealed that even under very acidic conditions, a high percent removal was accomplished, with 58% of Cu(II) and 77% of Pb(II) being removed at

pH 2.0. During the first contact time, the removal was rapid, and the adsorption data obtained at various contact times suited the PSORE well. Cu(II) had a maximum sorption capacity of 17.30 mg/g, while Pb(II) had a maximum sorption capacity of 107.52 mg/g. The inclusion of $MgCl_2$, NaCl, and KCl had no discernible effect on the removal of Cu(II) and Pb(II) utilizing ABn-AG. Cu(II) and Pb(II) were removed from ABn-AG via distinct binding sites, according to binary adsorption research. The removal of Cu(II) and Pb(II) only dropped by 10% after the same material was reused five times, demonstrating that ABn-AG is a highly resilient material that can be reused multiple times without losing its efficiency [64].

Studies have shown that sodium alginate and bentonite/ Fe_3O_4 nanoparticles may be employed to effectively adsorb lead ions. To that goal, researchers synthesized four sets of bentonite magnetic nanoparticles (at bentonite weights of 0.2, 0.4, 1, and 2 g) [98]. The produced magnetic nanoparticles were immobilized on alginate and the beads were prepared for Pb(II) ions elimination in the synthetic pollutant solution at various adsorbent doses, pH values, stirring rates, pollutant concentrations, and adsorption durations in the following stage. The results reveal that employing 0.1 g of beads in a solution pH of 7, an adsorption time of 8 h, and a stirring velocity of 100 rpm was the best condition for removing Pb(II). Furthermore, the beads' adsorption effectiveness for a 30 ppm Pb(II) solution was around 98%, and Pb(II) adsorption employing alginate magnetic beads followed the Freundlich isotherm model [99].

A composite material (CAM-D2EHPA) based on alginate and magadiite/di-(2-ethylhexyl) phosphoric acid was successfully created. FTIR and SEM-EDX techniques were used to characterize CAM-D2EHPA air-dried beads. The sorbent was employed to separate Pb(II) and Ni(II) from nitrate solutions, and the primary sorption parameters of contact time, solution pH, and beginning metal concentration were investigated. At pH 4, the beads recovered 94% of Pb(II) and 65% of Ni(II) from dilute metal solutions containing 10 mg/L (sorbent dosage: 1 g/L and contact time: 1 min). The Langmuir model fits the equilibrium data better, and a PSORE fit the kinetic profiles better. For Pb(II) and Ni(II), the greatest sorption capacities (at pH 4) were 197 mg/g. A dilute solution (0.5 M) of HNO_3 was used to regenerate the sorbent, which worked well. There were no significant variations in sorption uptake after 10 sorption/desorption cycles with the composite material [98].

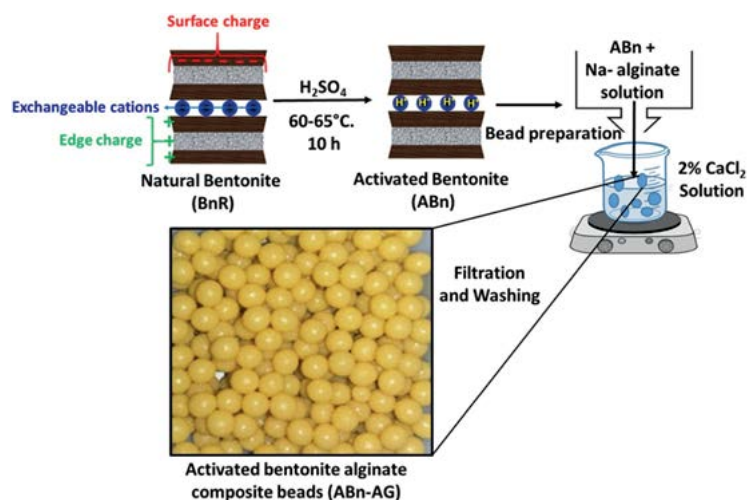


Fig. 6. Schematic representation of acid activation of bentonite and preparation of activated bentonite alginate composite beads [64]. Reproduced from Ref. 65, with permission (License Number 5356590991448) from Elsevier, 2022.

The sorption capacity of Cd(II) on three new sodium alginate (Alg) based nanocomposite beads; Alg-clay (Alg-C) beads, Alg-phosphate (Alg-P) beads, and Alg-activated charcoal (Alg-Ch) beads was examined on a batch scale, followed by a continuous flow reactor process [100]. Alg-Ch had the highest adsorption capacity (137 mg/g) when 1,000 mg/L of initial Cd(II) concentration was used. The adsorption equilibrium is comparable with the Langmuir isotherm, and the sorption capacity of Alg-nano-adsorbent beads is quite high, according to the isotherm results. The elimination of Cd(II) was well-fitted by PSORE kinetics, according to the models utilized to describe kinetic data. The maximum breakthrough times for the Alg-C, Alg-P, and Alg-Ch in the fixed bed column treatment were 30, 38, and 48 h, respectively. The SA-nano-adsorbent bead was found to be an excellent developed material as a nanocomposite for Cd(II) removal from wastewater in a continuous treatment process [100].

4.5. Gum-modified alginate

By regulating zeolite NaAlg dispersion in a calcium ion cross-linked binary xanthan gum–alginate hydrogel, novel hybrid NaAlg/xanthan gum (XG)–alginate composites were created [101]. Because XG moieties tended to interact with zeolite, avoiding particle agglomeration, pre-modification of zeolite NaAlg with natural XG enhanced particle dispersion. The composites' rich multi-dimensional characteristics were attributed to the binary combination of alginate and XG. Entrapped zeolites improved the composites' operation stability. Batch removal of Co(II) and Ni(II) was investigated. The sorption is optimum when the pH is 6.0. The sorption was well described by the Langmuir isotherm, with maximal sorption capacities of 43.9 and 81.3 mg/g at 323 K for Co(II) and Ni(II), respectively. Sorption kinetics followed a PSORE. The NaAlg/XG–alginate composite could be a potential candidate for removing Co(II) and Ni(II) from nuclear waste by adsorptive removal [101].

The accumulation of Ni(II) by gel beads of gellan gum (GG), alginate, carrageenan, agar, agarose, silica gel,

polyacrylamide, and two combinations of GG + agar in batch mode from diluted solutions was tested by Lázaro et al. [102]. All of the studied polymeric materials accumulated Ni(II), however, GG gel beads were the most stable, easy to produce, and accumulated the most Ni(II). Nickel accumulation was not affected by the pH of the solution. Other metal ions such as Cu(II), Co(II), Ni(II), Pb(II), Cd(II), and Zn(II) accumulated by GG gel beads reached equilibrium after 24 h. Pb(II) and Cu(II) were efficiently removed from the aqueous solution, with maximum metal sorption (q_{max}) of 0.85 and 0.75 mmol/g GG, respectively. $Pb > Cu > Ni = Zn = Co > Cd$ was the common q_{max} sequence. Except for Pb(II), a clear reduction in accumulation was found in an equimolar metal mixture sorption experiment (30%). Using 100 mM sodium citrate solution, the heavy metals were desorbed [102].

Alcohols, carboxylic acids, and amides, which are hydrophilic moieties, increase the stiffness and water-absorbing capacity of nanocomposite hydrogels (polymeric networks with a unique hydration property are known as nanocomposite hydrogels) [103]. The addition of a cross-linker to hydrogels during the manufacturing process improves their stability under high temperature, pH, and pressure conditions. Biodegradable, extremely hydrophilic, and mechanically strong natural polymer-based nanocomposite hydrogels such as gelatin, chitin, cellulose, pectin, carrageenan, starch, and alginate are often used to make nanocomposite hydrogels [103]. Nanocomposite hydrogels offer unique properties such as a high rate of swelling, selectivity, and stimulus sensitivity. In several nanocomposite hydrogels, Cu(II) adsorption capacity reached 30.35 mg/g, Pb(II) adsorption capacity reached 35.94 mg/g, and Zn(II) and Fe(II) adsorption capacity reached 94.34 mg/g. Furthermore, in the pH range of 5 to 7, most nanocomposite hydrogels demonstrated improved adsorption capability for contaminants. The nanocomposite hydrogels could also be regenerated and used again and again with success [103].

A sol-gel reaction was used to trap and condense amorphous silica into the network architectures of calcium

ion cross-linked alginate (CAIlg)–xanthan gum (XG) gel beads, resulting in an organic-inorganic bio-hybrid bead composite [71]. The effect of co-existing metal ions and particle size on Pb(II) adsorption by the composites was explored in a batch manner by adjusting the relevant parameters, which included solid/liquid ratio, contact time, pH, temperature, and influence of co-existing metal ions. The Langmuir isotherm model was better appropriate for the equilibrium data at 293 K, with a maximum adsorption capacity of 18.9 mg/g. It proved that Pb(II) adsorption was based on chemical binding, with intra-particle diffusion playing a role. Experiments carried out at 293 and 313 K allowed the thermodynamic characteristics of the adsorption process to be determined, namely ΔG° (5 kJ/mol), ΔH° (7.20 kJ/mol), and ΔS° (18.0 J/mol/K), revealing it to be a spontaneous and endothermic process. For composite regeneration and Pb(II) recovery, 0.5 M HCl was advised. The treatment of Pb(II)-bearing battery industrial effluent using a fixed bed experiment was attempted with an efficient degree of reversible performance over an extended time [71].

4.6. Sludge-alginate composite

In recent years, adsorbents made from solid waste materials have gotten a lot of interest. The goal of this investigation was to see how well a floating adsorbent made from drinking water treatment sludge could absorb heavy metals in the aqueous phase. Batch sorption experiments were used to explore parameters such as adsorbent concentration, contact time, solution pH, and the starting concentration of cadmium ions. The characterization of the adsorbent was done using SEM, FTIR, and elemental analytical techniques. The researchers looked into unmodified sludge, phosphoric acid modified sludge powder, and granular encapsulated sludges [104]. The adsorption capacity of all four sludge-based adsorbents towards Cd(II) was determined using the Langmuir model. The maximum cadmium load in the unmodified sludge increased to 40.3 mg/g in the phosphoric acid-treated material. The raw sludge absorbed 30 mg/g, slightly greater than the alginate gel-encapsulated sludge. After the adsorption process, the granular form of the encapsulated material made it easier to extract the adsorbent from the aqueous phase [104].

The kinetics of Cd(II), Zn(II), and Cu(II) removal by an activated sludge immobilized in 1.5% sodium alginate with 0.5% polyvinyl alcohol were determined by Filipkowska and Kuczajowska-Zadrozna [105]. The PSORE was discovered to govern the adsorption of metals from solutions of single metals and mixtures. Cadmium (96.10 mg/g) was most successfully absorbed in single metal solutions, but copper (37.38 mg/g) was most effective in metal mixes. It was also discovered that the presence of Cu(II) in a metal mixture hampered cadmium and zinc sorption [105].

4.7. Magnetic alginate-based sorbents

Recently, significant advances have been achieved in the development of magnetic alginate-based sorbents (i.e., the combination of alginate hydrogels with micro- and/or nanomagnetic particles (e.g., γ - Fe_2O_3 , Fe_3O_4 , CoFe_2O_4)

that can quickly respond to an external magnetic field, enabling their enhanced controllability. Fig. 7 shows a schematic representation of magnetic particles incorporated in alginate beads. The impact of the inserted magnetite nanoparticles (Fe_3O_4 NPs) on the physicochemical parameters, adsorption kinetics, and Cu(II) sorption mechanism was evaluated in calcium alginate-based adsorbents with magnetic and non-magnetic features (MCAIlg and CAIlg). XRD, SEM, TGA, and a superconducting quantum interference device magnetometer were used to characterize the sorbents [106]. The MCAIlg had a rough surface with a lot of protuberances, according to the SEM examination. The CAIlg had an amorphous form, according to the XRD examination. The MCAIlg had better thermal stability than the CAIlg, according to the TGA analysis. At room temperature, the MCAIlg were shown to be superparamagnetic. Copper ion adsorption tests on ABs and MCAIlg were also carried out. The MCAIlg and CAIlg have adsorption efficiency of 54.9 and 66.7 mg/g, respectively, for the same weight of the alginate matrix. A PSORE was used to track the adsorption kinetics, and the diffusion properties were important in controlling the adsorption kinetics. The adsorption equilibrium rate constant was found to be 1.98 104 g/mg min for CAIlg and 3.8 104 g/mg min for MCAIlg in the PSORE [106].

Sodium alginate, L-cysteine, CaCl_2 , and Fe_3O_4 were used as raw ingredients in another study to create an environmentally friendly magnetic composite MSAIlg [107]. Using simulated and real copper-containing electroplating wastewater, the effects of pH, coexisting ions, and contact time on Cu(II) adsorption performance were investigated. The following preparation conditions were found to be suitable in the single factor optimization experiments: sodium alginate concentration of 30.0 g/L, L-cysteine concentration of 6.0 g/L, CaCl_2 concentration of 2.5 g/L, and Fe_3O_4 concentration of 2.0 g/L. Cu(II) adsorption amount by MSAIlg increased significantly with increasing pH, and a high removal rate was maintained at pHs of 3.0–5.0. Copper(II) removal rate in electroplating wastewater achieved 94.02% when the pH was 5. The PSORE and the Langmuir isothermal model both predicted that adsorption was dominated by monolayer adsorption and regulated by chemical processes, with a maximum adsorption capacity of 175.45 mg/g. MSAIlg displayed outstanding magnetic responsiveness and was easily removed from the solution, according to the results of the characterization. Ion exchange and coordination between amino, carboxyl, and copper is the main adsorptions mechanisms [107].

In a different study, iron oxide particles that were produced *in-situ* were modified using alginate that was

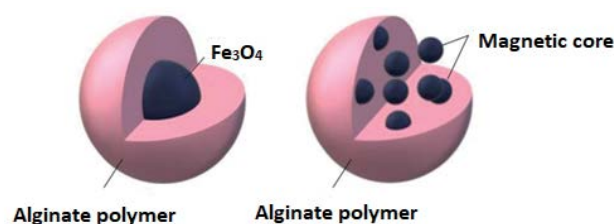


Fig. 7. Schematic representation of magnetic particles incorporation in alginate beads.

isolated from marine algal biomass [17]. This process made sure that all of the alginate adsorbent can be extracted from an aqueous solution after metal ion sorption. The ability of the resulting magnetic alginate (Alg-Fe₃O₄) to remove Cu(II), Co(II), and Zn(II) ions by sorption was evaluated. The optimal conditions were established as pH = 5.4, adsorbent dosage of 2 g/L, contact time of minimum of 60 min, and room temperature (23°C ± 1°C). The retention of metal ions was quantitative (99% for Cu(II), 89% for Co(II), and 95% for Zn(II)) when the concentration of metal ions was less than 0.80 mmol/L. The Langmuir model was found to be the best-fitted model for the equilibrium data, while sorption kinetics followed the pseudo-second-order model. Biosorption processes were spontaneous, endothermic, and accompanied by an increase in entropy [17].

Zinc ferrite-alginate beads (ZFN-Alg beads) were prepared and characterized using the FTIR, XRD, SEM, EDS, thermogravimetric-differential thermal analysis (TG-DTA), BET [65]. The pH of the adsorption of Pb(II) and Cu(II) ions on ZFN-Alg beads was examined in single and binary systems using batch mode as a function of contact time, pH, adsorbent dosage, and initial concentration at various temperatures. The PSORE well predicted the adsorption kinetics of Pb(II) and Cu(II) ions in both types of systems. The equilibrium data were strongly correlated by the Langmuir isotherm model among different isotherm models in single and binary systems. The maximal adsorption capacities of Pb(II) and Cu(II) ions for ZFN-Alg beads in single and binary systems were 108.8, 106.6, 68.6 and 48.0 mg/g, respectively. The computed adsorption thermodynamic characteristics for both types of systems suggested that the adsorption process was spontaneous and exothermic. The ability of ZFN-Alg beads to regenerate was tested in both types of systems for up to five cycles. In both types of systems, the results demonstrated that ZFN-Alg beads retained roughly 80% regeneration efficiency after five consecutive cycles [65].

Polluted waters are complex systems with a variety of toxins coexisting, making simultaneous cleanup a difficult process. To address this issue, sorbent with a unique mix of interfacial characteristics and diverse surface chemistry was developed by Yap et al. [108] to remove heavy metals. The bioinspired sorbent, graphene biopolymer foam (Alg-Fe₃O₄-rGO-4S), is engineered by combining alginate (Alg) and reduced graphene oxide (rGO) functionalized with tetrathiol and decorated with iron oxide nanoparticles to mimic the wetting micro-topology of a darkling beetle with a combined hydrophilic-hydrophobic surface (Fe₃O₄). Single pollutant removal is demonstrated, with adsorption capacities of 107.0 mg/g for Hg(II), 73.5 mg/g for Cu(II) [108].

Polysaccharide materials are limited as viable adsorbents due to their poor stability, low absorption, and recovery rate. By mixing carboxymethyl chitosan (CMC), sodium alginate (SAlg), and graphene oxide@Fe₃O₄, a novel composite adsorbent – the magnetic composite gel beads (CMC/SAlg/graphene oxide@Fe₃O₄) was created, which was then used to adsorb Cu(II), Cd(II), and Pb(II) from wastewater [109]. CMC/SAlg/graphene oxide@Fe₃O₄ beads' physicochemical properties were studied in depth. Due to the addition of graphene oxide@Fe₃O₄, the CMC/SAlg/graphene oxide@Fe₃O₄ magnetic gel beads separated readily from the wastewater and

showed increased stability. The adsorption of Cu(II), Cd(II), and Pb(II) on the magnetic gel bead were well fitted with the PSORE and Langmuir isotherm model, and the maximum adsorption capacity of Cu(II), Cd(II), and Pb(II) was 55.96, 86.28, and 189.04 mg/g, respectively, according to the adsorption experiments. Furthermore, the magnetic gel beads adsorb Pb(II) selectively. Furthermore, after five cycles, the magnetic gel beads still achieved 90% of the adsorption rates and demonstrated good adsorption efficiency in the simulated real environment. This study demonstrates that CMC/SAlg/graphene oxide@Fe₃O₄ magnetic gel beads as adsorbents have promising wastewater treatment capability [109].

Magnetic graphene oxide/alginate beads (MGO/CAIlg) were produced for competitive adsorption of Cu(II) [110]. The pH of a single system affects the adsorption of Cu(II) on MGO/CAIlg, with 5.0 being the optimal pH. The PSORE and the Langmuir isotherm model were shown to accurately represent Cu(II) sorption; the diffusion process with two stages was used to describe the adsorption process [110].

An ionic polymerization route was used to synthesize an adsorbent through cross-linking into CaCl₂ solution by dimerizing monomers via cation coordination. Fig. 8 highlights the detailed synthesis method used to prepare mesoporous magnetic polymer beads mesoporous alginate/ β -cyclodextrin polymer (HNTs-FeNPs@Alg/ β -CD) [30]. The adsorption capacity of HNTs-FeNPs@Alg/ β -CD was higher than that of raw halloysite nanotubes (HNTs), iron nanoparticles (FeNPs), and bare alginate beads. FeNPs induce the magnetic properties of adsorbent and metal-based functional groups in and around the hydrogel beads. Maximum adsorption capacities of Pb, Cu, Cd, Ni were 21.09, 15.54, 2.47, and 2.68, respectively. The adsorption and selectivity trends of heavy metals were Pb > Cu > Cd > Ni, despite electrostatic binding strength of Cd > Cu > Pb > Ni and covalent binding strength of Pb > Ni > Cu > Cd. It demonstrated that not only chemisorption but also physisorption acts as the sorption mechanism. The reduction in surface area, porosity, and pore volume of the expended adsorbent, along with sorption study results, confirmed that pore filling and intra-particle diffusion played a considerable role in removing heavy metals [30].

A new form of magnetic chitosan/sodium alginate gel bead (MCSB) was created using sodium alginate hydrogel as a skeleton in combination with chitosan and magnetic Fe₃O₄. The MCSB was used to investigate the adsorption of Cu(II) from aqueous solutions as a potential candidate for environmental application. The adsorption process was studied using various kinetics and isotherm models. A detailed examination of the adsorption mechanism was undertaken using Fourier transform infrared spectroscopy, field-emission scanning electron microscope, CHNS/O elements analysis, vibration magnetometer, and various ways of characterization. With a saturation magnetization of 12.5 emu/g, the MCSB had a good magnetic performance. The inclusion of chitosan introduced a significant number of nitrogen-rich groups, which contributed significantly to copper adsorption onto gel beads, according to elemental analyses. To attain equilibrium, the contact time required for adsorption was tuned at 120 min. The adsorption process accorded well with the Langmuir isotherm model and the PSORE, according to experimental results.

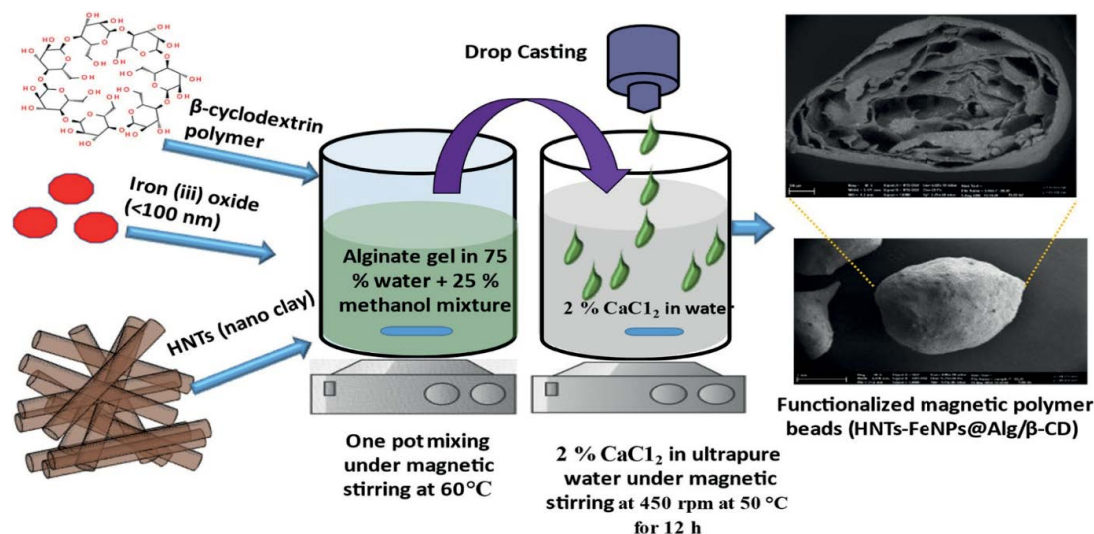


Fig. 8. Synthesis of functionalized magnetic hydrogel beads [30]. Reproduced from Ref. 30, with permission (License Number 5356600134264) from Elsevier, 2022.

MCSB's maximal predicted adsorption capacity for Cu(II) might be as high as 124.53 mg/g [111].

Copper in drinking water is a major environmental concern. In the realm of Cu(II) adsorption, composite materials based on alginate hydrogel have gotten a lot of attention. Modified chitosan/calcium alginate/ Fe_3O_4 hydrogel microspheres using NaOH solution (NACAF) to improve Cu(II) adsorption were investigated by Yi et al. [112]. The results show that modifying the adsorbent with NaOH solution enhances the mechanical strength and Cu(II) adsorption capability of original materials greatly. The adsorption mechanism is based on chelation and ion exchange, according to an XPS analysis. NaOH modified adsorbent has greater mechanical performance than the original one. The adsorption kinetics follows a PSORE. The Langmuir isotherm model best characterized the equilibrium data, and the calculated maximum equilibrium sorption capacity, q_m , for the NACAF is 261.31 mg/g, which is higher than that of the adsorbent before NaOH treatment (145.39 mg/g) [112].

Yi et al. [113] investigated if magnetic Fe_3O_4 nanoparticles could be encapsulated into calcium alginate-coated chitosan hydrochloride (CALgCM) hydrogel beads could remove Cu(II) and U(VI) ions from aqueous solutions. Copper(II) ions were attached to sorbents, as evidenced by SEM pictures and EDX spectra. During the entire sorption process, the sorption of Cu(II) followed the PSORE well and demonstrated a 3-stage intraparticle diffusion model, according to the sorption kinetic analysis. The Langmuir model best described equilibrium data, and the CALgCM composite hydrogel beads had estimated maximum adsorption capacities of 143.3 mg/g. The CALgCM adsorbent displayed good reusability, with no notable changes in adsorption capacity or structural stability after five cycles of use [113].

The Fe_3O_4 /SAlg (magnetite covered with sodium alginate) was prepared by Matei et al. [114]. SEM investigation revealed spherical magnetite particles wrapped into the

polymer with a diameter of 200 nm. The removal effectiveness of uncoated Fe_3O_4 (according to the adsorption Langmuir model) declined in the following order: Cr(VI) > Cu(II) > Zn(II) > Ni(II) > Cd(II). The adsorption phenomenon for the Fe_3O_4 /SAlg nanocomposite (45% w/w Fe in a polymer mass) is as follows: Cr(VI) > Cd(II) > Cu(II) > Zn(II) > Ni(II). The nanocomposite Fe_3O_4 /SAlg can be employed as an adsorbent with the same performance as uncoated Fe_3O_4 , but with the added benefit of stability in acidic industrial wastewaters [114].

The co-precipitation of graphene oxide with magnetite nanoparticles improves the magnetic field separation of a newly developed magnetite graphene oxide. Vu et al. [115] designed encapsulated magnetite graphene oxide inside a non-toxic alginate bead as a high-performance green chemical for the uptake of Cr(VI) and As(V) in water treatment applications (mGO/bead) due to the instability of magnetite graphene oxide under varied water chemistry circumstances. Although alginate has a minor contribution to metal ion uptake, it may limit the aggregation of magnetite graphene oxide powder, which has improved performance in extracting metals from water. The adsorption capacity of As(V) varied minimally over a pH range, whereas Cr(VI) adsorption varied with pH changes, which was explained by a local pH-controlled mechanism. The release of Fe(II) from Fe(III)-crosslinked mGO/beads aided induced hydrolysis and consequently improved Cr(VI) removal. The influence of co-occurring ions in a mixed contamination system (Cr(VI), As(V), Cu(II), Cd(II)) demonstrated an outstanding performance (80%–100% elimination) by the composite material for a complicated mixture of heavy metals [115].

The aerogel absorbent (Fe_3O_4 /SAlg-AR) is composed of Fe_3O_4 , alginate (SAlg), and industrial alkaline residue (AR) waste, resulting in a low-cost, easily recyclable spherical aerogel [116]. The magnetic aerogel spheres of the Fe_3O_4 /SAlg-AR are light-weight, have a loose porous structure, and have a mechanical strength ten times that

of typical SAlg aerogels, allowing them to withstand up to 20 compression-relaxation cycles. This high structural stability ensures the aerogel spheres' long-term integrity and floatability in water. Adsorption tests on Cd(II) ions indicated that equilibrium was reached in less than 2 h. The maximum adsorption capacity was 38.83 mg/g, which was higher than the maximum adsorption capacity recorded for typical SAlg aerogel adsorbents. After 5 cycles of adsorption–desorption, the aerogel spheres still retained an adsorption efficiency of 90% and were stable and reusable. The adsorption of Cd(II) to Fe₃O₄/SAlg-AR correlated well with the PSORE and the Langmuir isotherm model. FTIR, SEM-EDS, and XPS investigations revealed that Cd(II) adsorption to the Fe₃O₄/SA-AR aerogel was primarily mediated by OH complexation, electrostatic adsorption, and ion exchange. In conclusion, this study proposes a novel path for the synergetic resource usage of valueless and polluting alkaline residuals for heavy metal removal in wastewater [116].

The ability of magnetic alginate activated carbon (MAlgAC) beads to remove Cd(II), Hg(II), and Ni(II) from water in a mono-metal and the ternary system was reported by de Castro Alves et al. [117]. The MAlgAC beads' adsorption capability was greatest in the mono-metal system. The elimination effectiveness of such metal ions ranges between 20% and 80%, in the following order: Cd(II) > Ni(II) > Hg(II). The Freundlich isotherm fits best in the ternary system, while the Langmuir isotherm fits best in the mono-system. In the mono-metal system, the maximal Cd(II), Hg(II), and Ni(II) adsorption capacities derived from the Freundlich isotherm were 7.09, 5.08, and 4.82 (mg/g) (mg/L) ^{1/n}, respectively. The rivalry of metal ions for accessible adsorption sites resulted in lower adsorption capacity in the ternary system. Experiments on desorption and reusability revealed that the MAlgAC beads may be utilized for at least five successive adsorption/desorption cycles. These findings point to the MAlgAC beads being useful as an efficient adsorbent for the removal of heavy metals from wastewater [117].

Bio-magnetic membrane capsules (BMMCs) were created using a two-step titration gel crosslink approach, with polyvinyl alcohol and sodium alginate as the main encapsulating materials, to remove potentially harmful metals such as Pb(II) and Cd(II) from water [118]. The Langmuir isotherm model predicted the maximal monolayer adsorptive capacities for Pb(II) and Cd(II) at pH 6.5 to be 548 and 610.67 mg/g, respectively. The new BMMCs not only controlled PMNP oxidation but also sustained adsorptive removal over a wide pH range of 3–8, with electrostatic contact and ion exchange being the primary adsorption processes. The BMMCs were simply regenerated using 25% HNO₃ as an eluent for successful use in seven repeated cycles. As a result, BMMCs can be employed as an excellent sorbent or composite material to remove hazardous elements Pb(II) and Cd(II), indicating a high potential for enhancing water and wastewater treatment technologies [118].

Based on the utilization of a unique nanostructured material as an adsorbent, de Castro Alves et al. in another study [119] proposed an effective magnetic separation

approach for Cd(II) removal. This adsorbent incorporates magnetite nanoparticles (Fe₃O₄-NPs) produced by reverse coprecipitation with sodium alginate and activated carbon to form spherical structures by crosslinking Ca(II) ions with the charged alginate chains, known as magnetic calcium alginate activated carbon (MCAIlgAC) beads. The effect of experimental parameters such as pH, contacting time, adsorbent dosage, agitation type, and rotating speed on the effective removal of Cd(II) ions at an initial concentration of 250 mg/L was explored and optimized. At a pH of 6, the amount of Cd(II) adsorbed by MCAIlgAC beads increased with removal effectiveness of more than 90%. At an initial Cd(II) concentration of 150 mg/L, the maximum adsorption capacity attained was 70 mg/g of adsorbent, however, at 250 mg/L, the adsorption capacity decreased to 60 mg/g. Because of their ease of recovery from contaminated aqueous solutions, these studies demonstrated the MAAC beads' removal efficiency and prospective usage under real-world environmental circumstances [119].

A biologically toxic magnetic composite adsorbent (MSAL) with outstanding adsorption capacity for Pb(II) ions in solution was successfully constructed utilizing two non-biologically toxic materials, L-cysteine and sodium alginate [120]. The sorption process was tracked using a PSORE and a Langmuir isotherm model, indicating that adsorption was limited by a chemical process dominated by the molecular layer. According to the Langmuir isotherm model, the highest Pb(II) adsorption capacity was around 330 mg/g, which was superior to a wide range of other lead adsorbents. It was also discovered that the adsorption mechanism was mostly comprised of ion exchange and chelation between amino, carboxyl, and lead ions. After 5 cycles, the adsorption capacity dropped from 98.04% to 87.40% while remaining high. The iron ion concentrations in the adsorbed solution sample and the regeneration solution were 0.34 and 0.15 mg/L, respectively. Overall, the results indicate that MSAL is a viable reusable adsorbent for extracting Pb(II) from the solution [120].

The adsorption of Ag(I), Cr(VI), and Pb(II) onto iron magnetic nanoparticles, chitosan–magnetite nanocomposite, calcium alginate beads, and calcium alginate fungal beads (CAIlgFB) as a function of starting concentration, pH, and contact time were investigated [121]. The metal ion adsorption efficiency of chitosan–magnetite nanocomposite and calcium alginate fungal beads was much higher than that of iron magnetic nanoparticles and calcium alginate beads. The Freundlich model fit the data well, and the PSORE best represented the sorption kinetics [121].

The ability of composite hydrogel beads based on magnetic bentonite/carboxymethyl chitosan/sodium alginate (Mag-Ben/CCS/Alg) to adsorb copper ions in water was investigated. The results revealed that after 90 min of adsorption, Mag-Ben/CCS/Alg reached equilibrium, the removal rate of Cu(II) was 92.62 0.39%, and the maximum adsorption capacity was 56.79 mg/g (30°C). After recycling four times, the removal rate of Cu(II) via Mag-Ben/CCS/Alg remained above 80%. The Cu(II) adsorption process via Mag-Ben/CCS/Alg followed the quasi-second-order kinetic model and the Langmuir adsorption isotherm. The adsorption process was endothermic and spontaneous [122].

Copper(II) ions were removed from water using unique and very efficient magnetic alginate beads containing Fe₅C₂@SiO₂ nanoparticles (NPs) [123]. In the Cu(II) solution concentration of 200 mg/L, the maximum adsorption percent 97.4% was achieved in the pH range of 3–4 and the adsorbent dosage of 0.41 g/L. Furthermore, the highest adsorption capacity of silica-coated iron carbide alginate and alginate alone was evaluated. The addition of 1 mg of silica-coated iron carbide NPs to sodium alginate increased the adsorption capacity of Cu(II) ions almost twofold. With a maximum adsorption capacity of 37.73 mg/g for each layer, the Sips isotherm model best fits the experimental results. The PSORE was used to model the adsorption kinetics. These findings suggest that alginate Fe₅C₂@SiO₂ beads could be used to remove Cu(II) ions from aqueous solutions [123].

SEM and EDX were used to construct and analyze magnetic calcium alginate hydrogel beads (m-CAlgHBs, 3.4 mm average diameter) made of maghemite nanoparticles and calcium alginate [124]. The adsorption removal of Cu(II) from an aqueous solution by m-CAlgHBs was modeled and optimized using the response surface methodology. Adsorption studies were also carried out to see how pH (2.0–6.0), adsorbent dosage (2.0–6.0 g/L), and initial Cu(II) ion concentration (250–750 mg/L) affected adsorption. The optimum adsorption conditions were pH 2.0 and 2.0 g/L adsorbent dosage for 250 mg/L initial Cu(II) ion concentration. For a 500 mg/L starting Cu(II) ion concentration, the amount of Cu(II) adsorption after 6 h was as high as 159.24 mg/g. The PSORE better represented the adsorption process, according to the adsorption kinetics. Desorption tests revealed that chelation rather than electrostatic contact was the preferred mechanism for Cu(II) adsorption. In the fifth cycle, the percent removal of Cu(II) on m-CAlgHBs could still be kept at 73% [124].

The development of low-cost wastewater treatment technologies is critical for the efficient removal of poisonous heavy metals (including metalloids) such as As(V) and Cd(II). The entrapment of nanocrystalline MnO₂ in polymeric microcapsules of CAlg was used to make magnetic biopolymer (CAlg-MO) [125]. Batch studies were carried out to investigate the adsorption isotherms and removal kinetics of As(V) and Cd(II) under constant pH 6.5, temperature 25°C, various initial concentrations of 30–300 mg/L, and contact time 0–48 h. The PSORE (R^2 0.99) and Langmuir isotherm model (R^2 0.99) mathematically effectively explained the pseudo-equilibrium process, with the maximum monolayer sorption capacity of 63.6 mg/g for Cd on CABs-MO. After 12 h of contact, the As removal rate was higher in a single contaminant system (up to 6.5 mg/g) than in a combined contaminant (As(V) + Cd(II)) system (0.8 mg/g), albeit the difference was not significant for Cd (p 0.05; t -test). Through three to five regeneration cycles, the performance of 10 mM HCl as a regenerating agent was greater (for As(V) in contrast to Cd(II), p 0.05; t -test) to distilled water. As(V) a result, the obtained data convincingly demonstrate CAlg-MO as a promising adsorbent for extracting metal pollutants from wastewater. More research is needed to investigate the decontamination of developing pollutants using innovative composite beads with a variety of physicochemical characteristics [125].

5. Future perspectives

Further study on the mechanisms involved in pollutant uptake by different alginate-based adsorbents should be encouraged to prepare for the probable significant evolution of alginate-based adsorbents' future environmental applications. Optimizing current and developing new alginate-based composites with distinctive characteristics and novel functionality for targeted applications is another area that requires research. While methods like ultrasound and microwave will probably advance the development of new composites, systematic investigation of more efficient material combinations to enhance adsorption capacity and mechanical, chemical, and thermal stability when cross-linking with alginate beads is still possible. To create new alginate-based adsorbents for a variety of applications, encapsulation techniques may be directly applicable. Because free hydroxyl and carboxyl groups are widely distributed along the polymer chain backbone in alginate, future research on chemical modifications of these two types of functional groups that change the properties of alginate may be used to create new alginate-based composites for specific environmental applications. Future perspectives for sodium alginate-based adsorbents include the following:

- Sodium alginate has a relatively low mechanical strength and stability. As a result of calcium ion exchange, synthesized materials might decompose, which limits the regeneration of adsorbent. The preparation of porous sodium alginate materials is difficult, which limits the available adsorption sites and specific areas.
- Wastewater containing heavy metals usually has a highly complex composition. The adsorption of heavy metal ions could be adversely affected by other pollutants. Therefore, It is important in multimetallic solutions to separate target metal ions from competing metal ions. The usefulness of sodium alginate adsorbents would rise if they were capable of selectively absorbing specific metal ions.
- It would be desirable to improve sodium alginate-based adsorbent's porosity. In natural polysaccharide polymers, achieving an ordered pore size remains a challenge. The physical and chemical properties of sodium alginate constrain the format and amalgamation strategy for permeable adsorbents. The pore size and surface area of alginate-based adsorbent cannot be calculated by BET since the relatively low-temperature continuance for these materials. It is prescribed to discover a cost-effective template or synthesis strategy to improve the porous structure of the composite adsorbent.
- The combination of theoretical calculation and experiment is crucial in future research in both synthetic process and experimental design aspects. Theoretical calculations can save time in adsorbent design and synthesis by evaluating molecular structure, binding energy, and electron migration.

6. Conclusions

The physicochemical and adsorptive characteristics of several alginate-based composites have been compiled.

Excellent adsorption performance has been demonstrated by the alginate-based adsorbents toward heavy metal ions from aqueous solutions. The following goals are required to be accomplished by functionalizing alginate: when using alginate-modified adsorbents, there is a noticeable visible improvement in the adsorption capacity as the pH range is increased stability and improved selectivity of adsorption. Therefore, chemical modification may be used to accomplish the following goals: enhance biodegradation; improve the adsorption properties and the selectivity for each metal, and introduce completely new properties that are absent from the unmodified parent alginate. An example of this would be to increase the resistance of the ionic gel by adding covalent cross-linking. The physical/mechanical properties of alginate-based composites are typically improved over those of the unmodified parent alginate, but the biocompatibility of alginate in combination with the novel properties of the encapsulated materials frequently lends synergetic functionalities to the new derivatives. These include the simplicity of separation and regeneration following metal ion adsorption. Adsorption mechanisms for chemical adsorption include chemical reduction, electrostatic interaction, and ion exchange, while chemical reduction or photocatalytic reduction has also been observed. It is possible to create sodium alginate-based adsorbents with distinct adsorption processes by combining theoretical calculations with chemical characterization. According to the papers cited, the alginate-based adsorbent had an affinity that was higher for Pb, Cu, and Cd and moderate for the majority of the other cationic metals that were reviewed. It's important to note that there are very few studies of column experiments because fixed-bed studies are crucial for scale-up and actual application from an industrial standpoint. Additionally, only a small number of research examined the treatment of real wastewater, one of the most significant markers of performance in real matrices, and competitive adsorption was not thoroughly studied.

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