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A review on Alginate-Nanoparticle as a potential tool for managing water pollution



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HIGHLIGHTS

- Alginate-based hydrogels can incorporate much water due to their hydrophilic nature
- Alginate-based composites have unique structural forms like flat membranes, hollow fiber, microsphere etc.
- Alginate composites are demonstrated to control inorganic, organic, and pathogenic microbes from water streams
- Alginate is from plant source and could provide an edge over synthetic fossil fuel-based materials

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ABSTRACT

Sustainable source-based hydrogels are now paid much importance for managing water pollution due to their distinctive chemical and physical properties like hydrophilicity, biocompatibility, viscoelasticity, superabsorbancy, softness, fluffiness, and biodegradability. Alginate-based hydrogels can incorporate much water due to their hydrophilic nature. Water pollution often changes groundwater, resulting in the inability to use it. Alginate-based gels remove pollutants through adsorption/desorption, transport, and other conventional techniques. Alginate-based hydrogels can incorporate much water due to their hydrophilic nature. Their composites have been demonstrated to control different water pollutants like inorganic, organic, and pathogenic microbes from various water streams in unique structural forms like a flat membrane, hollow fiber, microspheres, gels, foams, nanofibers, Calcium and sodium alginate-based hydrogel along with other materials like activated charcoal, zeolite, bentonite, graphene, biochars and composites have been proved to be effective blend in managing heavy metal pollutants. This review summarizes the results obtained from the sustainable removal of contaminants from water through the alginate-based hydrogel and the challenges associated with it for practical application in the future.

1. Introduction

World population growth, industrialization, and economy lead to environmental pollution and health complications. Researchers are looking for new materials, techniques, and processes to minimize the discharge effects of pollution. Maximum area, i.e., more than 70% of our planet's oceans, is an important water source and other valuable materials (food, minerals, algae, etc.). Apart from water, salts, minerals, and nutrients, the waterfront area is also used as a medium to cultivate seaweeds. Algal polysaccharides exhibit a unique chemical structure and properties not commonly found in terrestrial plants. Eutrophication due to algal bloom is considered a major pollution of water resources. Therefore, developing a material vital for pollution control protects the environment from algal blooms. The development and use of sustainable material from marine resources (algae – third generation biomass) due to growing energy demand, depletion of fossil fuel reserves, global warming, and deteriorating environment. Due to the high structural polysaccharide and low lignin content, seaweed has an edge over other biomass. Polysaccharides derived from algal biomass are being studied as pollutant preventive/control agents in various physical (thin films, microspheres, gels, foams, hollow fibers, nanofibers, etc.) and chemical forms (native and composite). The current review summarizes the key impacts of marine polysaccharides on managing water pollution [1-4].

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Biopolymers (natural polymers) are derived from natural resources and can be degraded. Called marine resources, they represent two different types of polysaccharides: one derived from marine animals (chitosan, chitin) and other biopolymers (alginate, carrageenan, ulvan, cellulose, fucoidan) source are associated with algae Figure 1. Chitosan is one of the most researched biopolymers for pollution control, and our goal in the present review is to curb algae-derived polysaccharides, specifically alginate, which is summarized here.

2. Alginate

Alginate can be used in pure and compounded states to effectively combat biological, inorganic, and organic soils. Due to its low cost and high affinity through the gelation process, alginate is widely used in the biosorption of heavy metals, especially due to the involvement of the functional groups -COOH and -OH in the cross-linking process Figure 1.

Alginate gel and polymer composites are being studied for wastewater treatment (organic dyes, heavy metals, antibiotics). Similar polymer-based (poly urea) cross-linked Ca-alginate aerogel microbeads are adsorbents for organic and inorganic pollutants. Alginate hydrogels or beads were loaded with magnetic materials suitable for the wastewater treatment process Figures 2 and 3.

Figure 4 shows that the native aerogels of alginate have the following properties: they shrink in a very short time, have high stability in seawater, and can also have absorption capacity for oil and organic solvents. These aerogels promise to remove more inorganic and organic pollutants from aquatic environments such as seawater, river water, and industrial effluents [5].

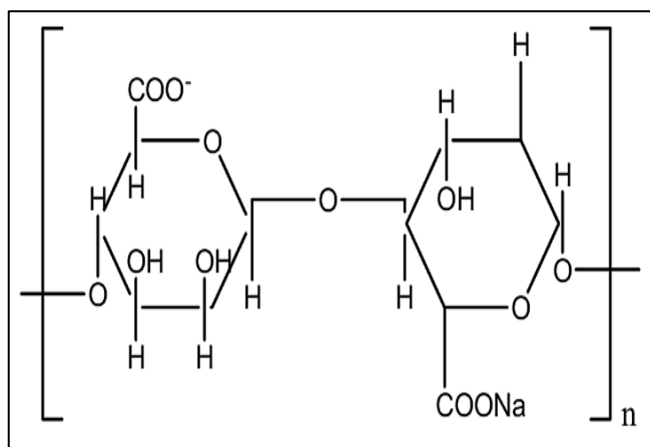


Figure 1: Chemical structure of sodium alginate

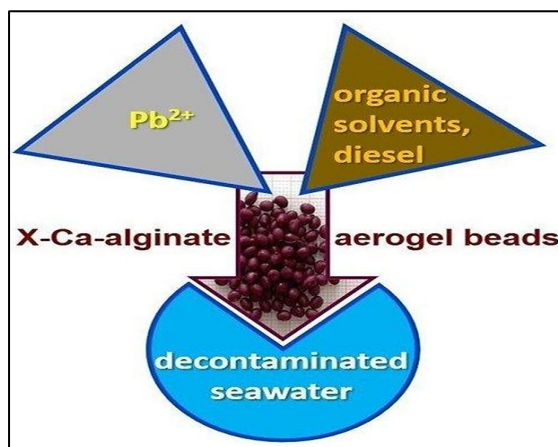


Figure 2: Aerogel beads preparation schematic representation [5]

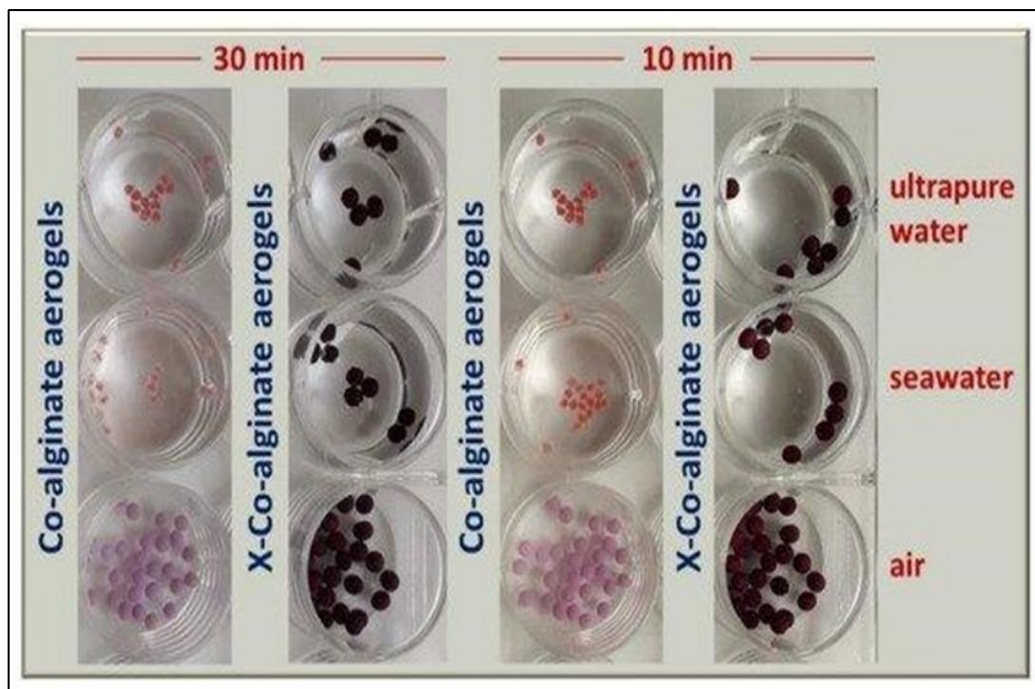


Figure 3: Optical photographs of different alginate aerogels [5]

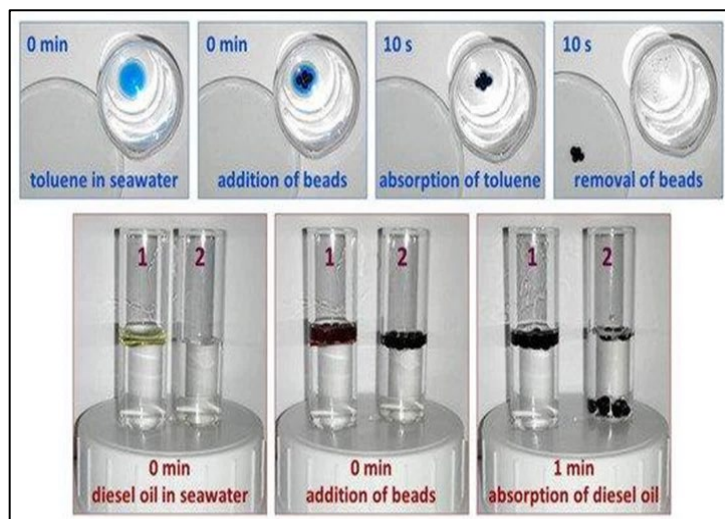


Figure 4: Selective uptake of toluene using X-Ca-alginate aerogel beads [5]

2.1 Role of Carbon-Based alginate composites as inorganic pollutants

The application of the alginate-based composites in managing inorganic pollutants is shown in Table 1. The uncrosslinked aerogel scaffold created by the freeze-dried ALG/GO blend is prepared. To enable a faster ionic cross-linking process, the mixture is then immersed in a CaCl_2 solution. During this exercise, the porous ALG/GO mixture hardens quickly due to a rapid reaction between calcium ions and alginate. The reproducible mechanical properties and the remarkable high flexibility of graphene oxide (GO) make it more suitable for use as a reinforcing filler. The developed air gel shows good flexibility and high mechanical strength thanks to the simple combined freeze-drying and ionic cross-linking method for incorporating GO into the alginate matrix. Its rough microstructure equipped with hydrophilicity ensures the excellent underwater superoleophobic properties of aerogel. The excellent salt tolerance of the aerogel is guaranteed by the high content of polysaccharides. The ALG/GO aerogel showed excellent salt tolerance, exceptional antifouling properties, and good underwater superoleophobia. In the case of oil/seawater separation, the separation of the prepared aerogel is achieved by the driving force of gravity [6].

The hydrogel beads of carboxylated cellulose nanocrystal sodium alginate (CCN-Alg) were synthesized by a simple cross-linking approach and characterized by FTIR spectroscopy, thermogravimetric analysis (TGA), zeta potential measurement, TEM, SEM, and XPS. Over 76% of the lead ions were adsorbed in two hours and reached equilibrium after one hour. An extreme adsorption capacity of 338.98 mg/g is found by fitting a Langmuir adsorption isotherm. This adsorption process is an endothermic process that follows a pseudo-second-order kinetic model. The spontaneity of the process is demonstrated by thermodynamic analysis. Acid treatment regeneration tests showed that in repeated Pb(II) adsorptions, CCN-Alg beads performed well with an adsorption capacity of 223.2 mg g^{-1} even after five repeated cycles, which suggests that CCN-Alg beads are potentially effective and sustainable adsorbent material for the application of wastewater treatment [7].

Due to the lack of mechanical alginate hydrogel and ability to fine-tune, it compromises its broader applications due to ion exchange between divalent and monovalent ions in a stable alginate solution. However, Zhuang et al., [8] improved alginate hydrogel's absorption capacity and mechanical strength by incorporating it with graphene.

The double network structure of the CaCl_2 mixed solution of GO and ALG in the neutral condition, with the calcium ions and sodium alginate forming hydrogel beads through cross-linking. GO accounted for only about 2% of the beads' weight. The mechanical stability of the alginate hydrogel was improved by Ca^{2+} and poly ethylenimine as polyelectrolytes to make the hydrogel stiff enough to act as a cell scaffold material [9]. In treating water contaminated with Mn(II), hydrogel beads provide a high surface area, biocompatibility from ALG, and thermal stability by GO inclusion. Hydrogel beads retain the functionality of GO, and they can be easily separated from the wastewater once absorption is completed, then regenerated and recycled.

Calcium alginate (CA) beads were made using sodium alginate cross-linked with CaCl_2 and used to remove Cd(II), Ni(II), Cu(II), and Zn(II) on an experimental basis. After drying, it was found that many canyons formed on the beads of CA's surface, thereby augmenting more adsorption sites. Thus, it can be understood from the trial that the CA beads showed a high capacity of removal efficiency Cu(II) selectively from the tetrametal mixture solution. According to the isotherm studies, the maximum uptake of Cu(II) was 107.53 mg/g, significantly higher than that of the other three heavy metal ions in the tetrametal mixture solution. The XPS analysis shows that the valency state of the four metal ions did not change during the adsorption process. Furthermore, the Cu(II) uptake rate on CA beads remained at 92% after five adsorption and desorption cycles [10]. ALG-AC beads prepared in a CaCl_2 solution adsorbed with strongly positively charged compounds and electrically neutral and low molecular weight compounds like p-chlorophenol [10].

Advances in nanotechnology help with water sanitation problems. Recently, to adsorb cadmium ions from a packed bed column and to meet the design parameters of adsorption in this continuous treatment process, the sorption properties were prepared by encapsulating a nano adsorbent with alginate selected from three natural materials (Moroccan clay, phosphate rock, Marble dust waste). Alginate and GO nanocomposites have also been used as adsorption materials for various substances, including heavy metals and dyes [11]. While alginate's negative groups can interact with positive groups, GO's oxygen groups

can interact with positively charged species such as metal ions and dyes, enhancing the ability of these nanocomposites to function as effective biosorbents. Furthermore, in addition to its high surface area, GO has a graphitized basal structure, allowing it to interact strongly with the aromatic moieties found in many organic molecules, such as drugs or dyes [11,12].

Based on the cross-linking process, SA-Phosphate (SA-P), SA-Clay (SA-C), and SA-Activated Carbon Beads are produced. The SA-Ch adsorption capacity was highest with 1000 mg L⁻¹ initial Cd(II) (137 mg g⁻¹). The isotherm results showed that the adsorption equilibrium is compatible with the Langmuir isotherm, and SA nano-adsorbent beads have a very high sorption capacity. It was assumed that second-order reaction kinetics would adequately describe the removal of Cd(II) in the models used to present kinetic data. SA-C, SA-P, and SA-Ch had maximum breakthrough times for fixed-bed column treatment of 30, 38, and 48 hours, respectively. According to the findings, SA nano adsorber beads are excellently designed as an effective nanocomposite for the continuous removal of cadmium from wastewater [11]. Due to its high capacity and selectivity for toxic heavy metals, the AC-AB adsorbent has enormous potential for application in drinking water treatment technologies.

Alginate gel and activated charcoal were combined to create an alginate bead containing activated charcoal. This adsorbent was manufactured, successfully removing heavy metal ions like Hg²⁺, Pb²⁺, Mn²⁺, Cd²⁺, Cu²⁺, Fe²⁺, Al³⁺, and Zn²⁺ and toxic organics like p-toluic acid from contaminated water. The adsorbent can be recycled using HNO₃ and eluent [13] through ten additional adsorption and desorption cycles.

The adsorption equilibrium properties of Cu and phenol on powdered AC, alginate beads, and alginate activated carbon beads (AAC) were reported by Kim et al., [14] examined Alginate beads were the most effective in adsorbing Cu(II) onto various adsorbents, followed by AAC beads and then AC. Alginate beads preceded AC beads in the phenolic chain. The Langmuir equation could be used to represent adsorption equilibrium data. Three different models were used to correlate multicomponent equilibrium data. The ideal adsorbed solution theory (IAST) provided the best fit. In addition, more Cu²⁺ was adsorbed on the AAC bead than phenol in the binary components [14].

Removal of toluene and zinc from water by impregnating alginate gel beads with powdered activated carbon (PAC) and synthetic zeolite also found to have the maximum adsorption capacity of the composite from the Langmuir isotherm was 4.3g kg⁻¹ or 13.0g kg⁻¹ as the research carried out Choi et al. [15], similarly, Do and Lee et al. synthesized a biochar alginate capsule to remove lead ions Pb(II) from an aqueous solution [16]. The maximum adsorption capacity for Pb(II) was 263.15 mg g⁻¹ at pH 5.0. and also created magnetite GO encapsulated with calcium alginate beads (mGO/beads) to adsorb Cr(VI) and As(V) from wastewater. As compared to carbon nanotubes and activated carbon, it was found that the mGO/bead retained its activity in the effluent and showed superior adsorption efficiency for both Cr(VI) and As(V). FeNPs embedded graphene oxide alginate beads (Fe@GOA) were created by blending zero-valent iron nanoparticles (FeNPs) in GO dissolved in alginate gel, which was then further reduced to give FeNPs embedded reduced to generate graphene oxide-alginate beads (Fe@GA beads) and used to remove Cr(VI) from aqueous [16].

The results showed that the best performance was obtained with 1% alginate and 1.52.0wt % FeO, with a maximum adsorption capacity of 34 mg/g [16]. Li et al. [17] prepared CNTs-CA composites by adding different SA and CNTs to a CaCl₂ solution. The results show that the specific surface area and pore size of the CA gel are 28 m² g⁻¹ and 0.06 cm³ g⁻¹, respectively. Because of their large pore size and high specific surface area, CNTs can contribute to the formation of microchannels in composites. The CNTs-CA composites had a specific surface area and pore size of 76 m² g⁻¹ and 0.37 cm³ g⁻¹, respectively. Cu(II) on CA gel had a higher adsorption capacity than CNTs under the same circumstances. The adsorption capacity of CA-gel was 52.1 mg g⁻¹ at equilibrium concentration and increased to 67.9mg g⁻¹ for CNTs-CA [17].

An adsorbent was prepared for the removal of As (V) by using potassium hydroxide-charcoal based apricot kernels (C), calcium alginate beads (G), and calcium alginate/charcoal composite beads (GC) and found that (G) adsorbent had more acidic functional groups than the other adsorbents [18] and also its adsorption capacity was found further higher when it was blended with (C), i.e. GC adsorbed 66.7 mg g⁻¹ at 30°C. The thermodynamic parameters and the endothermic spontaneous and physisorption processes were confirmed by the adsorption kinetic data, which follow a pseudo-second-order mechanism. Alginate/graphene double network hydrogel (GAD) underwent physicochemical modifications to increase its adsorption capacity and was compared to single network hydrogel (GAS).

The modified hydrogel had a more porous structure and functional groups than its conventional counterpart. Due to the lower swelling ratio of the GAD beads, Cu²⁺ and Cr₂O₇²⁻ have excellent adsorption capacities of 169.5 mg g⁻¹ and 72.5 mg g⁻¹, respectively. The coordination during metal ion adsorption to GAS and GAD was one of many significant interactions. Through complexation and coordination, the abundant -COOH in graphene and alginate showed a good affinity for Cr₂O₇²⁻ and Cu²⁺. There is an ion exchange interaction between Ca²⁺ in the alginate and Cu²⁺ in the solution, thereby increasing the removal of Cu²⁺. In addition, the development of the double network proves effective in improving adsorption [18].

Jiao et al. [19] prepared a sodium alginate/graphene oxide airgel (SAGO) through cross-linking and freeze-drying. The porous structure of the airgel is improved by the addition of GO, which has a positive effect on increasing strength, toughness, and absorbency. For this reason, the second-order pseudo-kinetic model and the Langmuir isotherm are better able to represent the adsorption process of SAGO. The maximum monolayer adsorption capacities for Cu²⁺ and Pb²⁺ are 98.0 mg/g and 267.4 mg/g, respectively [19].

2.2 Application of Alginate-Based composites for organic pollutants management

Dye is one of the major organic pollutants in water, and alginate-based airgel has great potential to manage it effectively. Different forms of SA/GO, like fibers, beads, and hydrogel nanocomposites, are effective bioabsorbents for the adsorption of dyes like methylene blue from wastewater. The ternary nanocomposite for removal of dye from water was synthesized by radical

polymerization of SA and acrylamide (AAM) in the presence of GO and subsequent cross-linking with Ca^{2+} and found very effective [19-21].

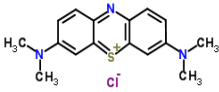
Ushadevi et al., [22] developed a nanocomposite-activated carbon/ Al_2O_3 nanocomposite (ANC) and checked its capacity to remove methylene blue (MB) from water contaminated and found that the adsorption mechanism follows the Freundlich isotherm model its removal capacity increases with increasing pH. According to the kinetic data, the dye adsorption follows a pseudo-second-order kinetic model. The adsorption process occurs spontaneously, as indicated by the negative value of G . The nanocomposite was processed into calcium alginate beads for the column study (CAB). To study the performance of the CAB, different influent concentrations of MB, pH, and bed depth were used, and the results were analyzed using the Thomas and BDST models. The column has a CAB adsorption capacity of 285.57 mg/g at pH 7 and a bed height of 10 cm, best fitting the BDST model. These results demonstrated the dye removal ability of carbon/ Al_2O_3 nanocomposites [22].

Various adsorbents were used, like calcium alginate beads (AB), sodium hydroxide-activated carbon-based coconut shells (C), and Calcium alginate/activated carbon composite beads (ACB). $C > \text{ACB} > \text{AB}$ had greater surface area and total pore volume, but AB was more acidic in its functional groups, which were higher than the other adsorbents [23]. The methylene removal capacity of these three adsorbents was checked in experiments, and results revealed that all three adsorbents required $\text{pH} > 6$ to prevent H^+ competition. As the dosage of the adsorbent increases, more dye is absorbed. The adsorption of the dye methylene blue follows a pseudo-second-order mechanism [23]. According to thermodynamic studies, the entire adsorption process was endothermic and spontaneous.

Benhouria et al. [24] prepared bentonite alginate, activated charcoal alginate, and activated charcoal bentonite alginate beads using a simple manufacturing technique to remove effluent from the methylene blue dye. After six regeneration cycles, the results of batch adsorption experiments showed that the maximum monolayer adsorption capacity of the activated carbon bentonite alginate beads was 756.97 mg g^{-1} at 30°C , with high flexibility in adsorption efficiency. Activated carbon blended with calcium alginate (ACCA beads) was used as an adsorbent to remove rhodamine 6G dye in a fixed dosage of 1 g l^{-1} . The results showed that a high percentage of the rhodamine 6G dye was adsorbed with these beads, and the factorial design of the experiments suggested that the dye concentration is a crucial element for the effective removal of the dye [25].

Hydrogel was made with a blend of sodium alginate (SA), innovative graphene oxide (GO), and polyacrylamide (PAM) through the radical polymerization of acrylamide (AAM) and SA in the presence of GO in an aqueous system, followed by ionic cross-linking of calcium ions and found that this hydrogel exhibited exceptional mechanical performance [26]. Including GO in the adsorbent significantly increased the adsorption capacities of the hydrogels for cationic dyes (R6G, MB, MG, and BG) and anionic dyes (CA, MO, BR, and RB). Li et al. prepared calcium alginate-graphene oxide composites and used them to remove methylene blue dye in batch adsorption experiments. Using the Langmuir isotherm equation, they found that the maximum adsorption capacity was 181.81 mg g^{-1} . It was discovered by monolayer adsorption that the adsorption reaction on the homogeneous surface of GO/CA was exothermic and spontaneous [27].

Table 1: Alginate-based composites in water pollution control

No.	Alginate - Composite material	Pollutants	Adsorption capacity	Observation
1	Hydrogel beads, CCN-Alg (HU et al. [7])	Pb(II)	338.98 mg/g	Pseudo-second-order kinetic model applied and fitted by the Langmuir model
2	Calcium alginate beads	Cu(II)	107.53 mg/g	Langmuir adsorption isotherm
3	Sodium Alginate + Clay beads, Sodium Alginate + Phosphate beads, Sodium Alginate + Activated Charcoal beads (Faissal et al. [11])	Cd(II)	137 mg/g	Langmuir adsorption isotherm
4	Alginate + activated carbon Beads (Part et al. [13])	Pb^{2+} , Mn^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , Fe^{2+} , Al^{2+} and Hg^{2+}	-	Reusable for 10 cycles
5	Alginate gel bead loaded with zeolite, activated carbon (Choi et al. [15])	Zn(II)	4.3 g/kg and 13.0 g/kg	Langmuir adsorption isotherm
6	Alginate + Biochar composite microcapsules (Do et al. [16]).	Toluene	263.158 mg/g	-
7	Sodium alginate + graphene oxide aerogel (Jiao et al. [19])	Pb(II)	98.0	-
8	Alginate + Activated carbon + Al_2O_3 (Ushadevi et al. [22])	Methylene Blue	267.4	Freundlich isotherm model
9	Alginate + activated carbon + Bentonite beads (Benhouria et al. [24])	Methylene Blue	116 mg/g	Langmuir adsorption isotherm
10	Calcium alginate + Graphene oxide composites (Li et al. [27])	Methylene Blue	756.97 mg g^{-1}	Langmuir adsorption isotherm
11	Alginate + Graphene Nanocomposite (Zhuang et al. [8])		169.5	-
		Cu(II)	72.5	

Using the traditional CaCl_2 curing method, acridine orange dye was adsorbed onto synthesized SA and GO-based porous beads. The larger pore size enhanced the adsorption process, allowing for faster ion diffusion. Hydrogen bonds between the hydroxyl groups and carboxyl SA and those of GO were investigated. Improved adsorption kinetics and the macroporous nanocomposites (with CaCO_3) were found better by adding GO than using simple SA beads. A bioadsorbent was developed with a mix of calcium alginate and multi-walled carbon nanotubes (CA/MWCNTs) to adsorb ionic dyes like methyl orange (MO) and methylene blue (MB), and it was found that MO and MB have increased adsorption capacity and speed on the bioadsorbent [28]. The second-order pseudo model fit the equilibrium adsorption data well, and Langmuir and Freundlich's isotherms were used to study the adsorption kinetics. According to the results, adding MWCNTs increased the adsorption capacity of MOs by 3-fold and increased the adsorption rate of MBs compared to native CA. Li et al. [29] prepared a composite fiber of calcium alginate and multi-walled carbon nanotubes (CA/MWCNTs) by wet spinning to serve as a bioadsorbent.

Due to the large surface area, MWCNTs were able to increase the adsorption capacity on CA/MWCNT composite fibers by about 14.13 mg g^{-1} MO fibers, showing that the Langmuir adsorption isotherm fits experimental results better than the Freundlich isotherm. According to investigations by Gong et al., [30]. The complex centrifugal separation process can be a limiting factor. Therefore, adding magnetic properties to a multi-walled carbon nanotube system will aid in the separation process. Besides improving mechanical properties, the introduction of GO also ensured good adsorption capacities for cationic and anionic dyes. This is due to the covalent and non-covalent adsorption of the dyes to the resulting GO-based composite hydrogels. On the one hand, the cationic dyes have several active components, such as amino and azo groups, which interact with the carboxyl groups of the hydrogel. On the other hand, the aromatic units in the dye molecules have strong interactions. Similarly, it was found that the introduction of a zeolitic imidazolate framework (ZIF-8) showed extremely high adsorption performance for the cationic dyes crystal violet (CV) and malachite green (MG) with high adsorption capacity [31,32].

2.3 Alginate-Based composites in disinfection of water

A new approach to water remediation combining biopolymers and nanoparticles has shown promise for treating water contaminated by bacteria. Although this type of conventional nanoparticle-based water disinfection faces numerous obstacles in terms of cost-effectiveness and application, it still has the potential to be used in water treatment applications. Point-of-use (POU) drinking water treatment systems have been developed since centralized drinking water treatment plants are not viable. Encapsulating sodium alginate with antimicrobial zinc oxide nanoparticles on bentonite and its bactericidal activity were prepared using surface water and artificial water containing *Staphylococcus aureus* [33]. The nanocomposites demonstrated excellent antimicrobial activity in just one minute, killing all bacteria in surface water with an initial bacterial concentration of $80 \text{ CFU } 00\text{mL}^{-1}$. In Table 2, it was shown that increasing the amount of nanocomposite and contact time improved inactivation. After 70 minutes of contact time with 0.5g of the nanocomposites and an initial bacterial concentration of 200 CFU ml^{-1} for synthetic water, no bacteria were found in the water [33].

The Nanocomposites can act as disinfectants and adsorbents to treat water loaded with bacteria. The bactericidal activity of nanocomposite is basically caused by bacteria adhering to its surfaces, probably due to their opposite charges. The leached Zn ions pierced the cell wall of the bacterium, resulting in cell lysis and death, and it was interestingly found that the amount of leached Zn^{2+} ions in water was within the permissible limits, which makes the nanocomposites suitable for disinfection. Nanocomposites are inexpensive to fabricate, making them suitable for point-of-use systems and enabling large-scale production. For portable alternative traditional water purification, silver nanoparticles (AgNPs)-alginate beads were successfully prepared for the dual purpose of disinfection and filtration by Lin et al., [34]. To test the antibacterial activity, the prepared composite beads were placed in a column of water containing *Escherichia coli*. Simultaneous Gelation Reduction (SGR), Adsorption Reduction (AR), and Nanoparticle Incorporation (NI) are three different methods for making composites, and all were found to have varying degrees of success in eradicating *E.coli*. disinfection [34].

According to the results, SGR beads are superior to the other two, shown in Figure 4. and demonstrated acceptable bactericidal performance with a relatively low material consumption rate. Beak et al. [35] created ZnO NP-alginate beads to kill antibiotic-resistant bacteria. The research findings of this experiment showed significant effectiveness. Alginate biopolymer serves as a dispersant and improves the electrostatic and repulsion in the process of inactivation bacteria. Also, it assists in maintaining a larger surface area while preventing nanoparticle aggregation. Therefore, ZnO NP-alginate beads have been demonstrated to be a versatile material for the disinfection and filtration of antibiotic-resistant bacteria [35].

Table 2: Bactericidal activity of alginate nanocomposites

Nature of water	Initial Bacterial concentration	Nanocomposite amount	Time of contact	Status
Surface water	80 cfu/100 ml	0.2g/100 ml of surface water	1 min	Inactivation of bacterial growth
Synthetic water	200 cfu/1 ml	0.2g/100 ml of synthetic water	120 mins	„
		0.5g/100 ml of synthetic water	70 mins	„
		1g/100 ml of synthetic water	1 min	„

2.4 Alginate- Ionic liquid composite for water treatment

For the removal of Hg(II) from contaminated water, a novel solid-phase extractant media was prepared by using ionic liquid and PVA-alginate matrix gel beads and found an adsorptive removal rate of 99.98%, the maximum Hg(II) ion adsorption capacity measured was 49.89 (0.11) mg/g at pH 5.8. Hg was preferred over Pb and Cu regarding the PVA/IL beads' selectivity for those ions [36]. The results of the second-order model following kinetic data indicated that PVA/IL beads could be effectively used as novel extractants to remove divalent mercury from aqueous solutions under simpler operating conditions. Tetraalkylphosphonium dicyanamide, or Cyphos IL-105, was biopolymerized and immobilized in alginate capsules to bind Cd(II) to HCl solutions effectively. Between Cd(II) and the phosphonium cation, there was a 1:2 ratio, and the sorption capacity was found to increase proportionally with ionic liquid content. The chemical reaction rate equation, or pseudo-second order [37], and Crank's equation, which measures resistance to intraparticle diffusion, accurately describe the uptake kinetic data. Rufato et al. [38] created chitosan/alginate and N, N-dimethyl chitosan/alginate-based adsorbents for removal of Pb(II) ions from wastewater and found it performed effectively at significant levels and it was also possible to recover and repurpose the used ionic liquid [38].

Cyphos Phosphonium ionic liquids and Cyphos ionic liquids (IL-111, IL-109, IL-105, and IL-101) were immobilized in alginate/gelatin composite capsules and tested for sorption of Cd(II). Since Cyphos IL-111 is typically solid at room temperature, the phase change makes the resin particle form large vesicles [39]. It was also found that the anionic components of the IL, like chloride, tetrafluoroborate, and dicyanamide, did not affect the sorption isotherms. Diffusion properties of adsorbents were improved by taking advantage of their intraparticle diffusion kinetic equation and creating highly porous foams as an alternative to resin beads. Alginate was immobilized using alkylphosphonium IL to bind Pd(II) from HCl solutions.

The batch hydrogenation of nitro phenols (NPs) and 4-nitroaniline (4-NA) was tested on the composite material using sodium formate/formic acid as the hydrogen donor (HD) post-chemical reduction of Pd(II). For 2-NP, 3-NP, 4-NP, and 4-NA, the effects of agitation, particle type, size, concentration, and pH on lead adsorption have been assessed. A polymer composite with a blend of gelatin and alginate by using resins immobilized with Cyphos IL-101, resins, which range in size and ionic liquid content (IL), have been used to remove mercury from HCl solutions irrespective of their concentration, it no effect on extraction. Thus, the ion exchange was used to recover metal (binding of HgCl₄²⁻). The effectiveness of the resins for recovering Hg(II) was demonstrated by sorption isotherms and uptake kinetics that adhered to pseudo-second order [40]. Tetraalkylphosphonium IL was used to strengthen the gel in highly porous discs by being immobilized in cellulose fibers and alginate as composites. These biopolymer composite discs have been used to immobilize Pd(II) by adsorption from HCl solutions. The metal reduction makes it possible to create a catalytic material that can successfully hydrogenate 4-nitroaniline into p-phenylene diamine while using formic acid. For eight consecutive catalytic runs, the kinetics of hydrogenation were achieved by the IL and compared with methanol-washed material (without the IL). Pd micro/nanoparticles can be stabilized by the composite's presence, preventing their release into the solution.

Alginate beads immobilized with ionic liquid function as sustainable and biodegradable adsorbent material. Separation Lead(II) ion from contaminated water was separated by using alginate (Alg) beads with ILs of [Bmim][PF₆], [Bmim][DCA] and [Bmim][NTf₂] and CaCl₂ as a cross-linker, the adsorption Pb(II) depends on the type and loading of the ionic liquid used and initial pH of the water contaminated with the Pb (II). The results of the experiments also showed that 25% Bmim DCA-impregnated alginate beads have the highest capacity for adsorption at pH 5.5. The research on alginate ionic liquid composites is still in the early stage and should be encouraged for a clean and sustainable environment [41].

The high adsorption performance was ascribed to the mesoporous/macroporous network-like structure and the availability of many active adsorption sites in the alginate-based hydrogel. The role of GO in creating the specific surface area and porosity has improved the removal of pollutants at higher levels. It has been reported that GO improved adsorption using NaAlg-acrylamide with high specific surface area (6.983 m²/g) and porosity (average pore diameter: 24.62 nm) as it was proven by comparison of the adsorption capacity of acrylamide/graphene NaAlg system with and without GO [42]. Inorganic nanomaterial-based NaAlg hydrogels have also increased the capability of removing pollutants. For instance, a nanocomposite hydrogel consisting of acrylic acid, NaAlg, and tetraamine copper (II) sulfate was developed by in-situ cross-linking for the adsorption of CV and malachite green (MG) due to improving the chemical interaction with the dye molecules while enlarging the surface area for adsorption, the NPs incorporated in the hydrogel facilitated dye adsorption [43]. Similarly, Maqbool et al. [44] reported that Congo red dye could be adsorbed and removed by sodium alginate and polypyrrole composites blended with algal biomass. Fluoride is a major water contamination and is often associated with fluorosis of teeth. Kumari et al. [45] proposed Fe₃O₄/graphene/alginate hydrogels for removing fluoride (F) ions from water. Alginate-based hydrogel was proven to be an excellent material for removing heavy metals. Santoso et al., [46] developed calcium alginate-exfoliated clay sponge composites to remove Cu²⁺ and Cr⁶⁺ ions from an aqueous solution.

3. Conclusion and perspectives

From the literature reports, it can be concluded that an alginate-based hydrogel can be one of the candidates for effectively removing pollutants like heavy metal ions, dye, and microbes from water. Further, incorporating nanomaterials like GO, ZnO, TiO₂, etc., greatly improves the adsorption performance of the hydrogel because the nanoparticles significantly improve the surface area and porosity of the hydrogel. Alginate-based hydrogels can incorporate a large amount of water due to their hydrophilic nature and unique structural forms like flat membranes, hollow fibers, microspheres, gels, foams, nanofibers, etc. Alginate, a green biopolymer extracted renewal seaweed, could provide an edge over synthetic fossil fuel-based materials and has huge potential to manage water pollution.

However, the main challenge in applying alginate-based hydrogel in water treatment is carrying out experimental procedures in practical applications and variable environmental conditions. The research that has been carried out is mostly at the laboratory scale. Therefore, research must be carried out at a large scale and develop pollutant-based application procedures. Though environmental conditions significantly impact adsorption behavior, it is rare to find the testing of the hydrogels for real water samples in the literature. The effectiveness of hydrogels under challenging environmental conditions must, therefore, be prioritized. Also, considerable efforts still need to be employed in the context of the circular economy, a market analysis of the alginate markets, and the production capacity of alginate-bearing seaweeds.

Author contributions

Conceptualization, D. Lakshmi, K. Radha, T. Azeez and Sh. Munisamy; writing—review and editing, D. Lakshmi, K. Radha, T. Azeez and Sh. Munisamy. All authors have read and agreed to the published version of the manuscript.

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Data availability statement

The data that support the findings of this study are available on request from the corresponding author.

Conflicts of interest

The authors declare that there is no conflict of interest.

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