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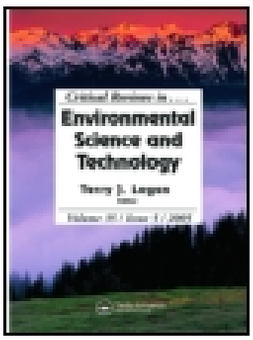

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Alginate-based composites for environmental applications: a critical review

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ABSTRACT

Alginate-based composites have been extensively studied for applications in energy and environmental sectors due to their biocompatible, nontoxic, and cost-effective properties. This review is designed to provide an overview of the synthesis and application of alginate-based composites. In addition to an overview of current understanding of alginate biopolymer, gelation process, and cross-linking mechanisms, this work focuses on adsorption mechanisms and performance of different alginate-based composites for the removal of various pollutants including dyes, heavy metals, and antibiotics in water and wastewater. While encapsulation in alginate gel beads confers protective benefits to engineered nanoparticles, carbonaceous materials, cells and microbes, alginate-based composites typically exhibit enhanced adsorption performance. The physical and chemical properties of alginate-based composites determine the effectiveness under different application conditions. A series of alginate-based composites and their physicochemical and sorptive properties have been summarized. This critical review not only summarizes recent advances in alginate-based composites but also presents a perspective of future work for their environmental applications.

KEYWORDS

Alginate; hydrogel; nanocomposites; dyes; heavy metals; antibiotics

1. Introduction

Achieving environmental goals while supporting robust economic growth demands innovative technologies for water and wastewater treatment (Gupta and Ali, 2012; Lim & Aris, 2014; Michael et al., 2013; Yagub, Sen, Afroze, & Ang, 2014). Adsorption technology has been considered as one

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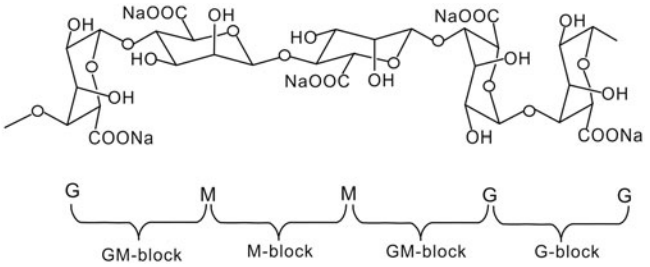

Figure 1. The molecular structure of sodium alginate (SA).

of the most effective and environmentally sound methods for remediating contaminants that are difficult to degrade in the environment (Ali, 2012; Ali and Gupta, 2006; Fu & Wang, 2011; Lim & Aris, 2014; Wan et al., 2018). Recently, various biomaterials have been developed for improving adsorption capacities, increasing environmental compatibility and operation efficiency as alternatives for conventional activated carbon (Burakov et al., 2018; Gupta, Carrott, Ribeiro Carrott, & Suhas, 2009). As a low cost and highly efficient absorbent, alginate-based composites have been extensively studied for the removal of heavy metals, industrial dyes, pesticides, antibiotics, and other pollutants in water and wastewater (Fomina & Gadd, 2014; Wan Ngah, Teong, & Hanafiah, 2011; Wang, Gao, & Wan, 2018b; Wang, Gao, Zimmerman, & Lee, 2018; Wang, Gao, Zimmerman, Zheng, & Lyu, 2018; Yagub et al., 2014).

Alginate is an anionic polysaccharide found in the outer cell wall of brown algae, such as kelps. The major component of alginate is alginic acid while sodium alginate (SA) is Na-salt of alginic acid, which is a polymer with abundant free hydroxyl and carboxyl groups distributed along the backbone chain of the polymer (Figure 1). The linear, anionic polysaccharide consists of two kinds of 1,4-linked hexuronic acid residues, namely β-d-mannuronopyranosyl (M) and α-l-guluronopyranosyl (G) residues, arranged in blocks of repeating M residues (MM blocks), blocks of repeating G residues (GG blocks), and blocks of mixed M and G residues (MG-blocks) (Yang, Xie, & He, 2011). Sodium alginate itself is nontoxic, stable in the environment with strong gelation, film-forming, and complexing abilities. The sodium alginate gel is soft and soluble in alkaline solution. It can go through an irreversible chemical process with polyvalent cations (except magnesium) to form a crosslinking bond, and finally the formation of a thermo-irreversible gel. For example, when Ca^{2+} is added to the SA solution, Ca^{2+} displaces part of H^{+} and Na^{+} to form a calcium alginate (CA) gel. Due to its nontoxicity, biocompatibility, and the ability to form crosslinks with cations, alginate has been utilized for encapsulation of chemical and biological compounds with a wide range of application in agriculture, food technologies, pharmaceutical cosmetics, chemical

engineering, environmental engineering, paper and textile industry, and many other areas.

Environmental applications of alginate hinge partly on the fact that the rich surface functional groups (e.g., carboxyl and hydroxyl) in alginate could capture metallic or cationic ions via ion exchange between the crosslinking cations and target pollutants such as heavy metals or dyes. However, alginate gel has disadvantages such as high rigidity and fragility with poor elasticity and mechanical properties (Thakur, Pandey, & Arotiba, 2016). Organic and inorganic alginate-based composites have been synthesized to enhance mechanical and thermal stability, and swelling properties of pure alginate gels (Thakur et al., 2016). These composites possess unique physicochemical properties and excellent biocompatibility. Over the past decade, alginate-based composites combining alginate gels and other polymers, natural and engineered nanoparticles, and microorganisms are extensively studied for the removal of pollutants from aqueous solution (Ali, Al-Othman, & Sanagi, 2015; Ali, Al-Othman, & Al-Warthan, 2016a; Ali, Al-Othman, & Al-Warthan, 2016b; Wang, Gao, & Wan, 2018a; Wang et al., 2018b; Wang, Gao, Zimmerman, & Lee, 2018; Zhao, Qin, & Feng, 2016). However, these studies are scattered, aiming to report the adsorption performance of specific composites. No comprehensive literature reviews on alginate-based composites as adsorbents for environmental applications are currently available.

The objective of this paper is to provide a systematic synthesis of the existing literature over the past two decades regarding environmental applications of alginate-based composites with respect to their adsorption capacities and experimental conditions. Most of these studies focus on the removal of dyes and heavy metals, as well as dozens of studies on antibiotics and other pollutants. This review starts with an examination of the synthesis of alginate-based composites and their special functionalities resulting from various materials encapsulated in alginate. Subsequently, the adsorption mechanisms and performance of different alginate-based composites for the removal of dyes, heavy metals, and antibiotics from aqueous solutions are reviewed. Future perspectives on application of alginate-based composites for environmental remediation is presented.

2. Synthesis of alginate-based composites as adsorbents

Properties and potential applications of alginate-based composites depend largely on their synthesis, i.e. physical and chemical crosslinking methods (Ching, Bansal, & Bhandari, 2017; Idris, Ismail, Hassan, Misran, & Ngomsik, 2012). Four common methods including ionic crosslinking, emulsification, electrostatic complexation, and self-assembly have been used

for synthesis of alginate-based composites (Akhtar, Hanif, & Ranjha, 2016; Mane, Ponrathnam, & Chavan, 2015; Paques, Van Der Linden, Van Rijn, & Sagis, 2014). Physically crosslinked hydrogels are synthesized by ionic interaction, crystallization, stereocomplex formation, hydrophobized polysaccharides, protein interaction and hydrogen bond. In contrast, chemically crosslinked hydrogels are synthesized by chain growth polymerization, addition and condensation polymerization and gamma and electron beam polymerization (Maitra & Shukla, 2014). These synthesis methods have their own advantages and disadvantages. The synthesis of physically crosslinked sodium alginate hydrogel is simple, and the conditions are gentle, but the gel strength is poor. The structural regularity of chemically crosslinked sodium alginate hydrogel is better, and the preparation conditions are more complicated, requiring complete removal of the unreacted crosslinking agents for post-treatment.

Sodium alginate contains a large number of functional groups, such as active hydroxyl group and carboxyl group along with its backbone chain and can be chemically modified by chemical crosslinking, esterification and etherification. The fundamental process involving gel formation is the interaction between sodium alginate and divalent cations (such as calcium ions) or cationic polymers. Sodium alginate has a -COO- group in the molecule. When a divalent cation is added to the sodium alginate solution, sodium alginate undergoes a cross-linking reaction, Na^+ from the guluronic acid (G) blocks is exchanged with these divalent cations to form a water-insoluble gel with a characteristic "egg-box" structure. Different cations show different affinity for alginate, the ability of sodium alginate to bind to multivalent cations follows the sequence of $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Co^{2+} > Ni^{2+} > Zn^{2+} > Mn^{2+}$ (Russo, Malinconico, & Santagata, 2007). In this ionic cross-linking process of sol-gel reaction, the solution concentration, pH value, and metal ion intensity all affect the stability, mechanical strength, shape and structure of the gel beads (Chan, Jin, & Heng, 2002).

In order to improve the performance and stability of alginate for environmental applications, various materials have been incorporated into alginate hydrogel (microspheres) (De-Bashan, Moreno, Hernandez, & Bashan, 2002; Hong et al., 2017; Rezaei, Haghshenasfard, & Moheb, 2017; Wang, Gao, Zimmerman, Zheng, et al., 2018; Zhuang et al., 2016). Synthesis of these composites typically starts with mixing the material with sodium alginate solution before the gelation of calcium alginate (Figure 2). A comprehensive review of the literature indicates that the materials encapsulated in alginate for environmental applications include activated carbon (AC), biochar, carbon nanotube (CNT), graphene oxide (GO), nanoparticle, magnetic materials and microorganism (Figure 2). Selection of the materials to

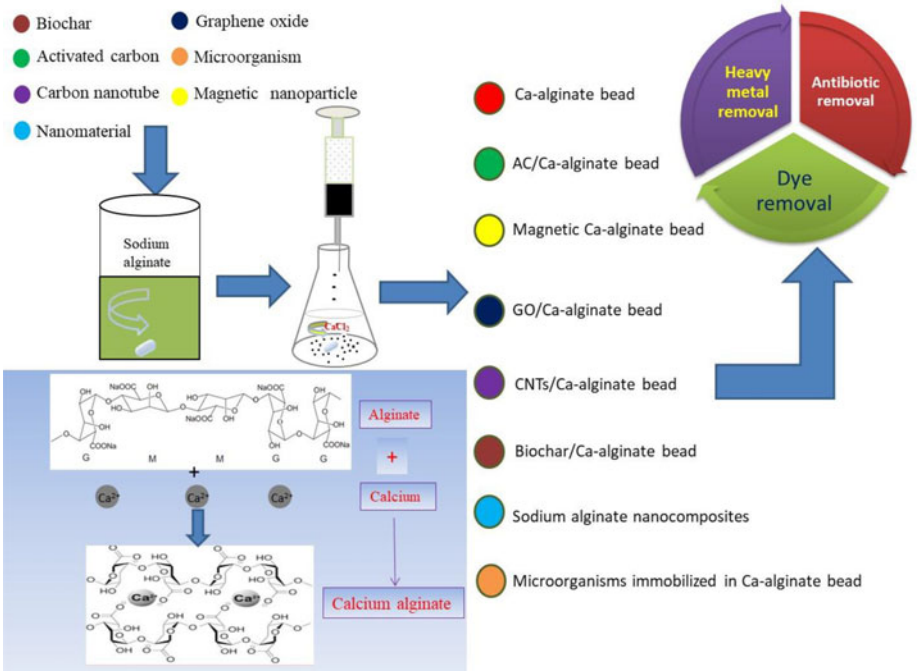

Figure 2. Fabrication of different alginate-based composites.

be encapsulated depends on the functionality of the material and the intended application so that synergetic benefits can be attained by the composite. While alginate-based composites typically exhibit enhanced physical/mechanical properties for bioengineering applications [24-25], a few other benefits achieved through fabrication are worth mentioning here.

First, alginate beards may serve as a stable matrix for other types of absorbents that are too fine in particle size and too difficult to separate from aqueous solution. These absorbents are typically carbon-based, such as AC, biochar, CNTs, and GO (Mohammadi, Khani, Gupta, Amereh, & Agarwal, 2011; Gupta, Nayak, Agarwal, & Tyagi, 2014; Robati et al., 2016). AC has been widely used for wastewater treatment (Maneerung et al., 2016). However, AC is mostly used as a fine powder, and the difficulty in separation and regeneration from the effluent may result in significant loss of the adsorbent. Biochar has been recently used as a cost-effective alternative of AC in water/wastewater treatment (Ahmad et al., 2014; Fang, Zhan, Ok, & Gao, 2018; Inyang et al., 2016; Mohan, Sarswat, Ok, & Pittman, 2014; Wang, Gao, & Fang, 2017). Biochar can be ball milled to increase its surface areas (Lyu et al., 2017; Lyu, Gao, He, Zimmerman, Ding, Huang, et al., 2018; Lyu, Gao, He, Zimmerman, Ding, Tang, et al., 2018). Like AC powders, ball milled biochar is difficult to separate from water due to its small particle size (Wang et al., 2018b; Wang, Gao, Zimmerman, Zheng, et al., 2018). CNTs and GO both have been intensively studied for removal

of organic and inorganic pollutants because of their unique structural features and large specific areas (Chen, Gao, & Li, 2015; Gupta, Kumar, Nayak, Saleh, & Barakat, 2013). The facts that GO disperses extremely well in water and CNTs are very small and form aggregates make it difficult to separate them from aqueous solution (Ding, Hu, Morales, & Gao, 2014; Inyang, Gao, Zimmerman, Zhang, & Chen, 2014; Tian et al., 2012; Wang, Yang, & Hsieh, 2010). Encapsulation of these carbonaceous materials into alginate hydrogels or beads offer ease of separation and regeneration for water/wastewater treatment (Wang et al., 2018a, 2018b; Wang, Gao, Zimmerman, & Lee, 2018; Wang, Gao, Zimmerman, Zheng, et al., 2018).

Second, fabricating magnetic materials and nanoparticles into alginate brings in nano-effects and magnetic technology into the composites while attaining excellent absorption performance and reducing the potential environmental risk of nanoparticles. Nanotechnology and magnetic technology have been increasingly used in water and wastewater treatment (Qu, Alvarez, & Li, 2013; Theron, Walker, & Cloete, 2008). Alginate/nanomaterial composites are blends of alginate and nanomaterials with enhanced adsorption capacity (Figure 3). Furthermore, a magnetic adsorbent (called magsorbent) can be developed by encapsulating magnetic functionalized nanoparticles in alginate beads along with different cross-linking agents (Lee et al., 2000; Russo et al., 2007). For example, incorporating maghemite with the alginate in bead form is very useful in isolation or recovery process (Idris et al., 2012). Magnetic technology has the advantage of simple operation and easy separation.

Third, alginate can serve a carrier of microorganisms to optimize the microbial processes for environmental and agricultural applications (Cohen, 2001; Covarrubias, De-Bashan, Moreno, & Bashan, 2012; Martins, Martins, Fiúza, & Santaella, 2013). Compared with the conventional suspension system, alginate microorganism composites offer a multitude of advantages, such as high biomass, high metabolic activity and strong resistance to toxic chemicals (An, Zhou, Li, Fu, & Sheng, 2008; Cai, Chen, Ren, Cai, & Zhang, 2011; Junter & Jouenne, 2004; Liu, Guo, Liao, & Wang, 2012). Moreover, immobilized microorganisms can be used several times without significant loss of activity (Rhee, Lee, & Lee, 1996). Therefore, alginate immobilized microorganism technology has received substantial attention for wastewater treatment (An et al., 2008).

3. Alginate-based composites as adsorbents for environmental applications

Alginate-based composites are fabricated as absorbents for both inorganic and organic contaminants. The adsorption mechanisms typically involve ion exchange and electrostatic interactions (Figure 4). Special functionalities

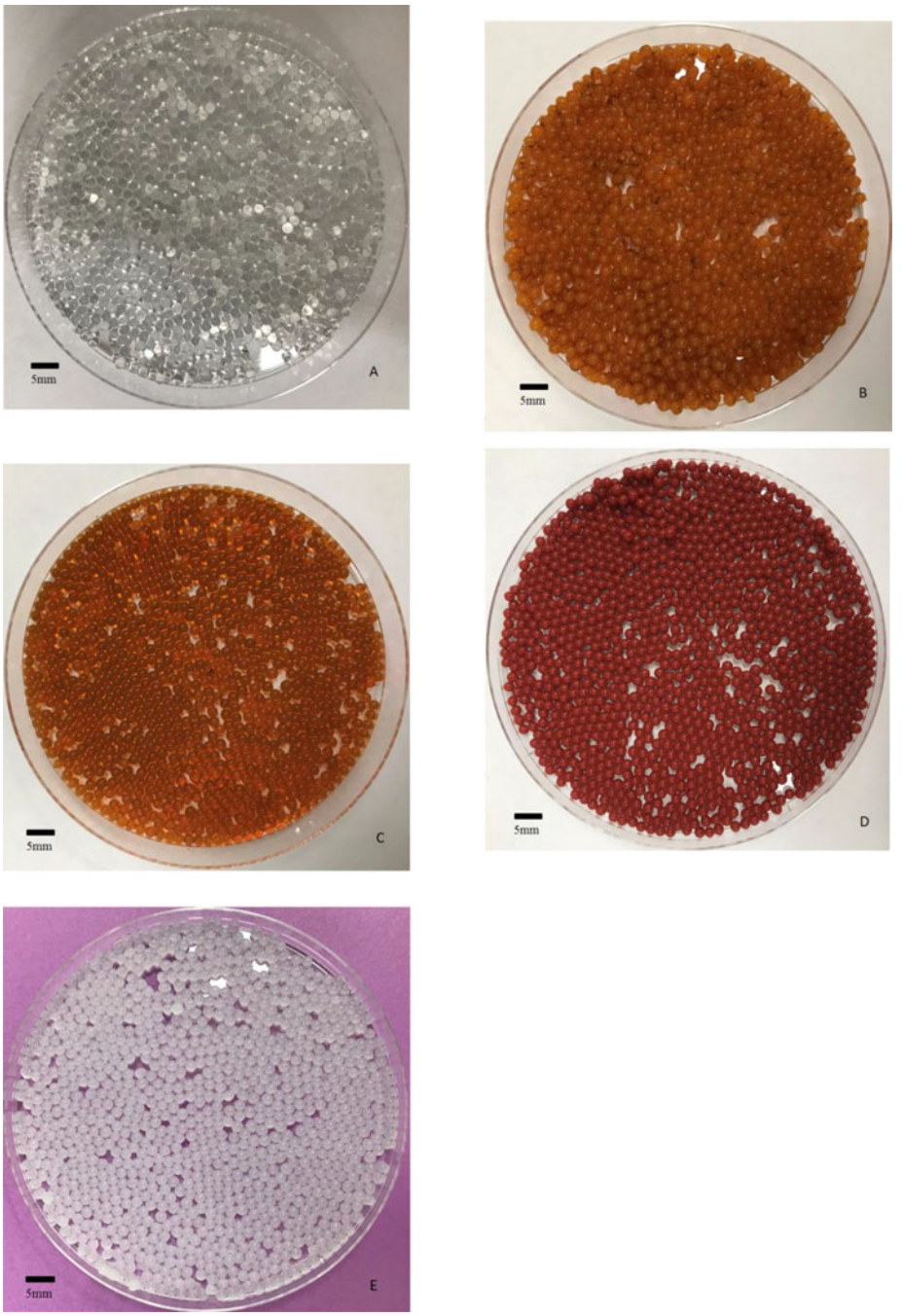

Figure 3. Photographs of different nanomaterial-alginate hybrid beads. Ca-alginate beads (A); Zero-valent iron nanoparticle-alginate composite beads (B); Silver nanoparticle-alginate composite beads (C); Fe_2O_3 nanoparticle-alginate composite beads (D); MgO nanoparticle-alginate composite beads (E).

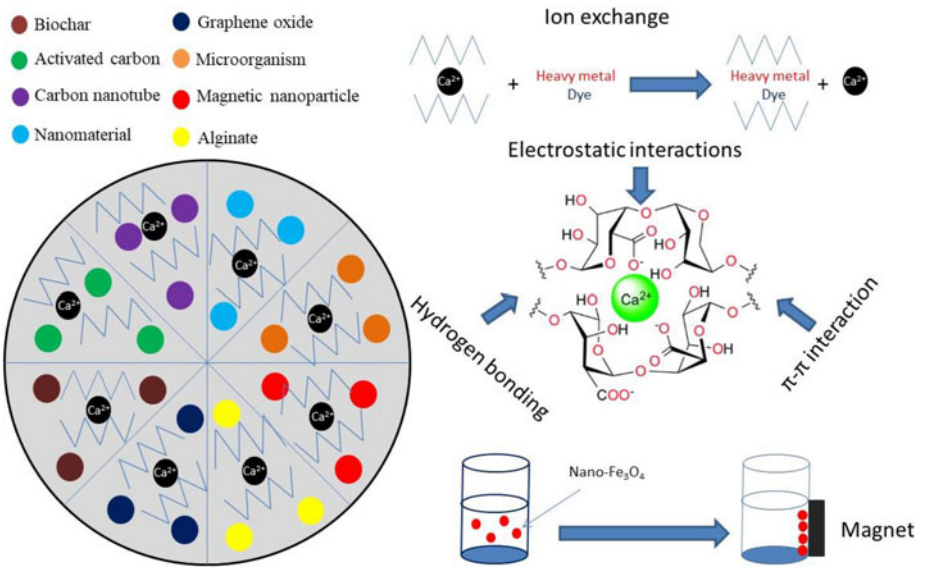

Figure 4. Adsorption mechanisms of different alginate-based composites on organic and inorganic contaminants in water.

of encapsulated materials may bring in other benefits depending on the needs and applications. This section is intended to discuss the performance and mechanisms of various types of composites for the removal of dyes, heavy metals, and antibiotics.

3.1. Dyes

Dyes are intensely colored complex organic compounds which have been heavily used in the textile industry. Release of processed dye wastes into the aquatic environment may result in harmful impacts on human health and the environment. The most obvious impact is the reduction of light penetration, thereby affecting the primary productivity of aquatic ecosystems. Some dyes and their derivatives are toxic to aquatic plants, fish, and shell fish. The removal of dye from wastewater is largely based on the adsorption technique whereby the dissolved dye is adsorbed by the sorbent (Fang, Gao, Mosa, & Zhan, 2017; Fang, Gao, Zimmerman, Ro, & Chen, 2016; Gupta & Suhas, 2009; Robinson, Mcmullan, Marchant, & Nigam, 2001; Zhang & Gao, 2013). Alginate itself is an excellent sorbent for dye removal. The potential use of pure calcium alginate beads for removal of black dyes was studied in a dynamic batch mode by Aravindhan et al. (Aravindhan, Fathima, Rao, & Nair, 2007). The adsorption isotherm suggested a Langmuir adsorption capacity of 57.70 mg g^{-1}. The performance of alginate-based composites for dye removal is summarized in Table 1 for a subset of studies. Each type of the composites is highlighted below.

Table 1. Alginate-based composites for the removal of synthetic dyes from aqueous solution.

Adsorbent	Adsorbate	Adsorption capacity (mg g^{-1})	pH	Temperature (°C)	Ref
GO/CA fibers	Methylene blue	181.81	5.4	25	(Li et al., 2013)
Calcium alginate beads	Basic black dye	57.70	4.0	30	(Aravindhan et al., 2007)
Graphene/alginate nanocomposite	Methylene blue	2300	8.0	25	(Zhuang, Yu, Chen, & Ma, 2016)
Alginate-halloysite nanotube	Methylene blue	250	—	35	(Liu, Wan, et al., 2012)
CA/MWCNTs	Methylene blue	606.1	—	25	(Sui et al., 2012)
CA/MWCNTs	Methyl orange	12.5	—	25	(Sui et al., 2012)
CA/AC beads	Methylene blue	892	—	20	(Hassan, Abdel-Mohsen, & Fouda, 2014)
CA/AC beads	Methylene blue	730	—	40	(Hassan, Abdel-Mohsen, & Fouda, 2014)
AC–bentonite–alginate beads	Methylene blue	756.97	—	30	(Benhouria et al., 2015)
AC–bentonite–alginate beads	Methylene blue	982.47	—	40	(Benhouria et al., 2015)
AC–bentonite–alginate beads	Methylene blue	994.06	—	50	(Benhouria et al., 2015)
Sodium alginate- Fe_3O_4	Malachite green	47.84	7.0	25	(Mohammadi et al., 2014)
AC/CA beads	Rhodamine 6G	—	—	—	(Annadurai et al., 2002)
Alginate/polyaspartate beads	Methylene blue	700	—	25	(Jeon, Lei, & Kim, 2008)
Alginate/polyaspartate beads	Malachite green	350	—	25	(Jeon et al., 2008)
Magnetic alginate beads	Methylene blue	22.06	6.7	—	(Rocher et al., 2008)
Magnetic alginate beads	Methyl orange	0.65	6.7	—	(Rocher et al., 2008)
Magnetic alginate beads cross-linked with epichlorohydrin	Methylene blue	261.73	—	—	(Rocher et al., 2010)
Magnetic alginate beads cross-linked with epichlorohydrin	Methyl orange	6.55	—	—	(Rocher et al., 2010)
CABI nano-goethite	Congo red	181.1	3.0	25	(Munagapati & Kim, 2017)
SA/n-TiO_2	Direct Red 80	163.9	2.0	25	(Mahmoodi, Hayati, Arami, & Bahrami, 2011)
SA/n-TiO_2	Acid Green 25	151.5	2.0	25	(Mahmoodi et al., 2011)
Activated organo-bentonite/SA	Methylene blue	414	—	23	(Belhouchat, Zaghouane-Boudiaf, & Viseras, 2017)
Activated organo-bentonite/SA	Methylene orange	116	—	23	(Belhouchat et al., 2017)
Methylcellulose/CA beads	Methylene blue	336.7	—	20	(Li et al., 2016)
Silver nanocomposite hydrogel	Methylene blue	213.7	—	Room T	(Devi, Kumar, & Kumar, 2016)
Montmorillonite/CA composite	Basic red 46 (BR46)	35	—	—	(Hassani et al., 2015)
SA/poly(N-vinyl-2-pyrrolidone) beads	Reactive red-120 (RR),	116.82	—	25	(Inal & Erduran, 2015)
Magnetic ferrite nanoparticle–alginate composite	Basic Blue 9 (BB9)	106	—	25	(Mahmoodi, 2013)
Magnetic ferrite nanoparticle–alginate composite	Basic Blue 41 (BB41)	25	—	25	(Mahmoodi, 2013)
Magnetic ferrite nanoparticle–alginate composite	Basic Red 18 (BR18)	56	—	25	(Mahmoodi, 2013)
SA/poly(N-vinyl-2-pyrrolidone) beads	Cibacron brilliant red 3B-A	73.3	—	25	(Inal & Erduran, 2015)
SA/poly(N-vinyl-2-pyrrolidone) beads	Remazol brilliant blue R	55.28	—	25	(Inal & Erduran, 2015)
Alginate–montmorillonite composite beads	Methylene blue	181.8	—	40	(Uyar, Kaygusuz, & Erim, 2016)

3.1.1. Activated carbon/alginate beads

Recent studies have shown that AC immobilized into calcium alginate removed a significant amount of dyes from wastewater (Hassan, Abdel-Mohsen, & Fouda, 2014). Benhouria et al. prepared bentonite-alginate beads, activated carbon-alginate beads, and activated carbon-bentonite-alginate beads via a simple fabrication method to remove methylene blue

(MB). The results showed that maximum monolayer adsorption capacity of activated carbon-bentonite-alginate beads was 756.97 mg g^{-1} at 30 °C with high resilience on adsorption efficiency after six regeneration cycles (Benhouria, Islam, Zaghouane-Boudiaf, Boutahala, & Hameed, 2015). Annadurai et al. studied batch adsorption equilibrium of Rhodamine 6 G using activated carbon incorporated into calcium alginate beads and obtained high percentages of adsorption of Rhodamine 6 G (Annadurai, Juang, & Lee, 2002).

Although the activated carbon and alginate composite processes excellent adsorption properties for dyes, the cost and reuse of activated carbon is still of concern. In order to make the activated carbon-alginate beads a magnetically separable adsorbent, the magnetic beads were prepared with a high magnetic sensitivity under an external magnetic field [31]. This provides an easy and efficient way to separate the beads from aqueous solution.

3.1.2. Graphene oxide/alginate composites

The GO and alginate biopolymer composites offer great potential for dye removal from wastewaters. For example, Yin et al. successfully fabricated graphene oxide (GO)/sodium alginate (SA)/polyacrylamide (PAM) (GO/SA/PAM) composite hydrogels for adsorption of cationic dyes (R6G, MB, MG, and BG) and anionic dyes (CA, MO, BR and RB) (Fan, Shi, Lian, Li, & Yin, 2013). In addition, Fan et al. fabricated a novel graphene oxide (GO)/sodium alginate (SA)/polyacrylamide (PAM) ternary nanocomposite hydrogel through free-radical polymerization of acrylamide (AAm) and SA in the presence of GO in an aqueous system followed with ionically cross-linking of calcium ions. The GO/SA/PAM ternary nanocomposite hydrogel exhibited excellent adsorption properties for water-soluble dyes. After introducing GO, the dye adsorption capacities of the hydrogel were significantly improved (Fan et al., 2013). Li et al. prepared the calcium alginate-GO composites and found that the maximum MB adsorption capacity obtained from Langmuir isotherm equation was 181.81 mg g^{-1}. The adsorption reaction was exothermic and spontaneous in nature, occurring on the homogenous surface of GO/CA by monolayer adsorption (Li et al., 2013).

3.1.3. Carbon nanotubes (CNTs)/Ca-alginate beads

Carbon nanotubes (CNTs) have been intensively studied as a potential material to be used in a variety of applications based on their specific physical and chemical properties (Wang, Gao, Zimmerman, & Lee, 2018, Gupta, Kumar, Nayak, Saleh, & Barakat 2013; Gupta & Saleh 2013). Sui et al. investigated the adsorption of methylene blue (MB) and methyl orange

(MO) ionic dyes onto calcium alginate/multi-walled carbon nanotubes (CA/MWCNT) composite fibers with varying MWCNTs content and pH values. The results showed that an introduction of MWCNTs increased the adsorption capacity of MO by 3 times, and enhanced the adsorption rate for MB compared to that of native CA (Sui et al., 2012). Li et al. prepared the CA/MWCNTs composite fiber to remove MO anionic dyes and the results illustrated that the introduction of MWCNTs obviously increased the adsorption capacity of MO, reaching about 14.13 mg g^{-1} (Li et al., 2012). Although the adsorption capacity increased using CNTs, the tedious centrifugation separation process might be a limiting factor and thus introducing magnetic properties into multi-wall carbon nanotube system will help with the separation process (Gong et al., 2009).

3.1.4. Other alginate nanocomposites

In addition to GO and CNTs, alginate has been blended with other natural and engineered nanoparticles to form nanocomposites to enhance the adsorption capacity (Tesh & Scott, 2014; Wang et al., 2018a, 2018b; Wang, Gao, Zimmerman, Zheng, et al., 2018). Mohammadi et al. prepared superparamagnetic sodium alginate-coated Fe_3O_4 nanoparticles for removal of malachite green (MG) from aqueous solutions. The maximum adsorption capacity obtained from Langmuir isotherm equation was 47.84 mg g^{-1} (Mohammadi, Daemi, & Barikani, 2014). Liu et al. prepared a new kind of porous beads by immobilizing halloysite nanotubes with alginate and found that the maximum MB adsorption capacity of about 250 mg g^{-1}. After 10 successive adsorption-desorption cycles, the removal efficiency of MB could be kept above 90% (Liu, Wan, et al., 2012). The alginate gel beads populated by halloysite nanotubes improved their ability to capture the dye so that they can have important implications for the enhancement of controlled adsorption. Compared to the unloaded gel beads, the hybrid gel beads are very effective and efficient for removing positively charged dye from the aqueous phase with enhanced properties (Cavallaro, Gianguzza, Lazzara, Milioto, & Piazzese, 2013).

Some novel synthesized composites showed great promise in removal of dyes. Nano-sized montmorillonite (MMT)/calcium alginate (CA) composite synthesized by Hassani et al. removed basic red 46 (BR46) in aqueous solution with the maximum adsorption capacity of about 35 mg g^{-1} (Hassani, Soltani, Karaca, & Khataee, 2015). Wang, Wang, and Wang (2013) prepared a series of NaAlg-g-p(AA-co-St)/organo-I/S nanocomposite absorbents to remove methylene blue (MB) and found that the nanocomposite can rapidly adsorb MB with an adsorption capacity of 1843.46 mg g^{-1}. TiO_2 immobilized in a Ca-alginate bead retained its photoactivity during all of the experiments and the TiO_2-gel beads presented good stability in

water for maintaining its shape after several uses (Albarelli, Santos, Murphy, & Oelgemöller, 2009). Impregnated calcium alginate beads with nano-goethite (CABI nano-goethite) removed Congo red (CR) from an aqueous solution, the maximum monolayer adsorption capacity was 181.1 mg g^{-1} at pH 3.0 and the adsorption process was endothermic and favored at high temperature (Munagapati & Kim, 2017).

3.1.5. Magnetic Ca-alginate beads

A series of studies have reported that alginate beads containing magnetic nanoparticles and activated carbon (AC-MAB) can selectively remove two dyes with different charges: positively charged MB and negatively charged methyl orange (MO). The adsorption capacity of beads was found to be higher than non encapsulated AC for MB and of the same order of magnitude for MO. The AC-MAB system selectively and strongly adsorbs MB due to the presence of carboxylate functions of both alginate and magnetic nanoparticles through ionic exchange with calcium ions (Rocher, Siaugue, Cabuil, & Bee, 2008).

Rocher et al. prepared another magnetic alginate beads by an extrusion technique and crosslinked with epichlorohydrin which contains both magnetic nanoparticles and activated carbon (Rocher, Bee, Siaugue, & Cabuil, 2010). With the addition of magnetic properties, the beads can be easily recovered or manipulated by an external magnetic field. Two mechanisms can be explained the adsorption process: (1) a hydrophobic adsorption onto encapsulated activated carbon which depends neither on the electrical charge of the dye, nor of the solution pH; (2) an ionic exchange between the positively charged dye and calcium ions and sodium ions, the counter ions of the carboxylate functions of both alginate and citrate-coated magnetic nanoparticles (Rocher et al., 2010).

Rosales et al. studied the decolorization of dyes under electro-Fenton process using Fe alginate gel beads and found that around 98-100% of dye decolorization was obtained for both dyes by an electro-Fenton process in successive batches (Rosales, Iglesias, Pazos, & Sanromán, 2012). Mahmoodi synthesized magnetic ferrite nanoparticle-alginate composite used to remove dyes from the binary system. The maximum dye adsorption capacity of MFN-alginate was 106 mg g^{-1}, 25 mg g^{-1}, and 56 mg g^{-1} for BB9, BB41, and BR18, respectively (Mahmoodi, 2013).

3.1.6. Microalgae immobilized in Ca-alginate beads

Immobilization of microbial cells in alginate beads has received increasing interest for dye removal. Chen et al. developed an efficient sol-gel method for fabricating alginate-silicate organic-inorganic gel beads for immobilization

of *P. luteola* cells and demonstrated the usefulness of such immobilized cells system in azo dye decolorization. The results indicated that the alginate-silicate matrix showed improvement over other synthetic or natural polymer gel matrices for immobilizing *P. luteola* in decolorization of Reactive Red 22 (Chen & Lin, 2007). Enayatzamir et al. studied the ability of white-rot fungus *Phanerochaete chrysosporium* immobilized on Ca-alginate beads to decolorize different recalcitrant azo dyes. The results showed that the MnP secreted by the fungus played the main role while adsorption was found to be negligible except for the dye BB in this decoloration process (Enayatzamir, Alikhani, Yakhchali, Tabandeh, & Rodríguez-Couto, 2010). Daâssi et al. found that the immobilization of *P. laccase* into Ca-alginate beads improved its thermal and storage stabilities and the immobilized *P. laccase* exhibited efficient textile dye decolorization in several successive batches (Daâssi, Rodríguez-Couto, Nasri, & Mechichi, 2014).

3.2. Heavy metals

Heavy metals in wastewater of industry and mining enterprises are of great environmental concerns due to their low toxicity thresholds and cumulative biological effects (Inyang et al., 2012; Xue et al., 2012; Zhou et al., 2013). It is extremely expensive to remove heavy metals from wastewater and reduce their toxicity in the environment. Several low-cost adsorbents and biopolymers, such as alginate and chitosan extracted from microalgae, shrimp, crab, and fungi are known to bind metal ions and could be used for heavy metal removal from wastewater (Babel & Kurniawan, 2003; Zhou et al., 2014; Zhou, Gao, Zimmerman, & Cao, 2014; Zhou et al., 2013). Alginate is rich in carboxyl, hydroxyl and other active functional groups, which can react with heavy metals through ion exchange or complex reaction. Therefore, it can be used as adsorption material to remove heavy metals. The performance of alginate-based composites for heavy metal removal is summarized in Table 2. Each type of the composites is highlighted below.

3.2.1. Ca-alginate beads

Alginate with a high M/G ratio, extracted from *Laminaria digitata*, was evaluated for Cu(II), Cd(II) and Pb(II) sorption in acidic solutions, in the form of calcium cross-linked beads. The high M/G ratio of alginate extracted from this algal species is most likely the determining factor for the increased adsorption capacity of the investigated metals, and the mannuronic acid in particular is responsible for the ion exchange mechanism. The presence of carboxyl groups in the alginate structure enhances the adsorption of many metal ions compared with other adsorbents. There are

Table 2. Alginate-based composites for the removal of heavy metals from aqueous solution.

Adsorbent	Adsorbate	Adsorption capacity (mg g^{-1})	pH	Temperature (°C)	Ref.
Biochar-alginate beads	Cd(II)	9.73	6.0	—	(Roh et al., 2015)
Graphite nano carbon beads	Co(II)	11.63	5.0	Ambient T	(Jung et al., 2015)
Graphite nano carbon beads	Ni(II)	11.48	5.0	Ambient T	(Jung et al., 2015)
Chitosan coated calcium alginate	Ni(II)	222.2	5.0	Room T	(Vijaya, Popuri, Boddu, & Krishnaiah, 2008)
Alginate–chitosan hybrid gel beads	Cu(II)	8.38	3.5	25	(Gotoh, Matsushima, & Kikuchi, 2004b)
Alginate–chitosan hybrid gel beads	Cd(II)	6.63	3.5	25	(Gotoh et al., 2004b)
Alginate–chitosan hybrid gel beads	Co(II)	3.18	3.5	25	(Gotoh et al., 2004b)
Iron oxide loaded alginate beads	As(V)	0.0226	7.0	—	(Zouboulis & Katsoyiannis, 2002)
Waste metal (hydr)oxide in CA beads	As(III)	126.5	8.0	20	(Escudero, Fiol, Villaescusa, & Bollinger, 2009)
Waste metal (hydr)oxide in CA beads	As(V)	41.6	8.0	20	(Escudero et al., 2009)
CA/GO beads	Cu(II)	60.2	—	—	(Algothmi, Bandaru, Yu, Shapter, & Ellis, 2013)
Biochar-alginate capsule	Pb(II)	263.158	5.0	27	(Do & Lee, 2013)
CA beads from Laminaria digitata	Cu(II)	88.95	4.5	25	(Papageorgiou et al., 2006)
CA beads from Laminaria digitata	Cd(II)	130.77	4.5	25	(Papageorgiou et al., 2006)
CA beads from Laminaria digitata	Pb(II)	374.67	4.5	25	(Papageorgiou et al., 2006)
Orange peel cellulose immobilized CA beads	Cu(II)	166.7	—	28	(Lai, Thirumavalavan, & Lee, 2010)
Orange peel cellulose immobilized CA beads	Pb(II)	128.2	—	28	(Lai et al., 2010)
Orange peel cellulose immobilized CA beads	Zn(II)	156.25	—	28	(Lai et al., 2010)
Banana peel cellulose immobilized CA beads	Cu(II)	163.93	—	28	(Lai et al., 2010)
Banana peel cellulose immobilized CA beads	Pb(II)	121.95	—	28	(Lai et al., 2010)
Banana peel cellulose immobilized CA beads	Zn(II)	183.85	—	28	(Lai et al., 2010)
Ca-alginate beads	Cu(II),	84.39	4.5	25	(Papageorgiou, Katsaros, Kouvelos, & Kanellopoulos, 2009)
Ca-alginate beads	Cd(II)	141.97	4.5	25	(Papageorgiou et al., 2009)
Ca-alginate beads	Pb(II)	360.11	4.5	25	(Papageorgiou et al., 2009)
Sodium alginate	Cu(II)	167.1	4.5	—	(Wang, Lu, & Li, 2016)
Sodium alginate	Cd(II)	179.0	4.5	—	(Wang, Lu, et al., 2016)
Sodium alginate	Pb(II)	435.3	4.5	—	(Wang, Lu, et al., 2016)
Polyvinyl alcohol (PVA)- SA beads	Cu(II)	0.69	—	—	(Cai et al., 2016)
Halloysite/alginate nanocomposite beads	Pb(II)	325	5.0	25	(Chiew et al., 2016)
Polyvinyl alcohol (PVA)- SA beads	Cd(II)	0.52	—	—	(Cai et al., 2016)
Polyvinyl alcohol (PVA)- SA beads	Pb(II)	0.60	—	—	(Cai et al., 2016)
Ca-Fe beads	As(V)	352	—	—	(Min & Hering, 1998)
SA-hydroxyapatite-CNT beads	Co(II)	347.8	6.8	21	(Karkeh-Abadi, Saber-Samandari, & Saber-Samandari, 2016)
Fe_0-Fe_3O_4 nanocomposites embedded polyvinyl alcohol (PVA)/sodium alginate	Cr(VI)		5.0	30	(Lv et al., 2013)
Magnetic alginate beads	Pb(II)	100	4.7	Room T	(Bée et al., 2011)
Magnetic alginate beads	Pb(II)	50	7.0	30	(Idris et al., 2012)
Alginate-montmorillonite/polyaniline nanocomposite	Cr(VI)	29.89	—	—	(Olad & Farshi Azhar, 2014)

(*continued*)

Table 2. Continued.

Adsorbent	Adsorbate	Adsorption capacity (mg g^{-1})	pH	Temperature (°C)	Ref.
Bio-polymeric beads	Cr(VI)	0.833	6.0	—	(Bajpai, Shrivastava, & Bajpai, 2004)
Fe_3O_4@Alg-Ce magnetic beads	Cr(VI)	9.166	5.0	30	(Gopalakannan & Viswanathan, 2015)
Fe_3O_4@Alg-Ce magnetic beads	Cr(VI)	11.069	5.0	40	(Gopalakannan & Viswanathan, 2015)
Fe_3O_4@Alg-Ce magnetic beads	Cr(VI)	12.503	5.0	50	(Gopalakannan & Viswanathan, 2015)
Chitosan–alginate beads	Cu (II)	67.66	4.5	Room T	(Ngah & Fatinathan, 2008)
Microgel/SA composite	Cu(II)	46.39	—	—	(Zhao et al., 2016)
Alginate activated carbon beads	Phenol	96.0	3	25	(Kim et al., 2008)
Alginate activated carbon beads	Phenol	85.6	7	25	(Kim et al., 2008)
Alginate activated carbon beads	Phenol	69.6	10	25	(Kim et al., 2008)
Nanochitosan/SA/microcrystalline cellulose beads	Cu(II)	43.32	—	—	(Vijayalakshmi, Gomathi, Latha, Hajeeth, & Sudha, 2016)
Magnetic nanocomposite beads	Cu(II)	72.99	6.0	25	(Bakr et al., 2015)
Graphene/alginate double-network nanocomposite	Cu(II)	169.5	4.0	—	(Zhuang et al., 2016)
Graphene/alginate double-network nanocomposite	Cr(VI)	72.5	4.0	—	(Zhuang et al., 2016)
Sodium alginate/graphene oxide aerogel	Cu(II)	98.0	5.0	30	(Jiao et al., 2016)
Sodium alginate/graphene oxide aerogel	Pb(II)	267.4	5.5	30	(Jiao et al., 2016)
Nanohydroxyapatite–alginate composite	Pb(II)	270.3	5.0	Ambient T	(Googerdchian et al., 2012)
Halloysite nanotube–alginate hybrid beads	Cu(II)	74.13	—	—	(Wang et al., 2014)
Silica nanopowders/alginate composite	Pb(II)	83.33	5.0	—	(Soltani et al., 2014)
Alginate activated carbon bead	Zn(II)	135	6.8	32	(Choi et al., 2009)
Alginate activated carbon bead	Toluene	215	6.8	32	(Choi et al., 2009)
Alginate Pleurotus ostreatus	Pb(II)	121.21	6.5	25	(Xiangliang, Jianlong, & Daoyong, 2005)
White-rot fungus Trametes versicolor in CA bead	Cd(II)	120.6	6.0	25	(Arıca et al., 2001)
Lentinus sajor-caju immobilized Ca-alginate	Cd(II)	123.5	6.0	25	(Bayramoglu et al., 2002)
Alginate-Ayous wood sawdust (Triplochiton scleroxylon)	Cd(II)	6.21	—	—	(Njimou, Măicăneanu, Indolean, Nanseu-Njiki, & Ngameni, 2016)
CA immobilized Phanerochaete chrysosporium	Cd(II)	85.4	6.0	25	(Kaçar et al., 2002)
CA immobilized Phanerochaete chrysosporium	Hg(II)	112.6	6.0	25	(Kaçar et al., 2002)
Fe_3O_4 nanoparticles embedded SA	Cd(II)	97.8	6.2		(Jiao, Qi, Liu, Wang, & Shan, 2015)
CA immobilized *Phanerochaete chrysosporium*	Pb(II)	355	7.0	25	(Yakup Arıca et al., 2003)
CA immobilized *Phanerochaete chrysosporium*	Zn(II)	48	7.0	25	(Yakup Arıca et al., 2003)
Spirulina platensis TISTR 8217 immobilized in alginate	Cd(II)	70.92	7.0	26	(Rangsayatorn et al., 2004)
Ca-alginate immobilized wood-rotting fungus	Hg(II)	403.2	6.0	20	(Arıca et al., 2001)
Ca-alginate immobilized wood-rotting fungus	Zn(II)	54.0	6.0	20	(Arıca et al., 2001)
Ca-alginate immobilized wood-rotting fungus	Cd(II)	191.6	6.0	20	(Arıca et al., 2001)

(*continued*)

Table 2. Continued.

Adsorbent	Adsorbate	Adsorption capacity (mg g^{-1})	pH	Temperature (°C)	Ref.
Ca-alginate immobilized-algal beads	Hg(II)	116.8	5.0	25	(Bayramoğlu, Tuzun, Celik, Yilmaz, & Arica, 2006)
Ca-alginate immobilized-algal beads	Cd(II)	88.6	5.0	25	(Bayramoğlu et al., 2006)
Ca-alginate immobilized-algal beads	Pb(II)	384.4	5.0	25	(Bayramoğlu et al., 2006)
Bacterial consortia immobilized in alginate beads	Cr(VI)	657	3.0	30	(Samuel et al., 2013)
Alginate–goethite beads	Cr(III)	20.67	3.0	20	(Lazaridis & Charalambous, 2005)
Alginate–goethite beads	Cr(VI)	23.38	3.0	20	(Lazaridis & Charalambous, 2005)
Scenedesmus quadricauda immobilized Ca-alginate beads	Cu(II)	75.6	5.0	25	(Bayramoğlu & Yakup Arıca, 2009)
Scenedesmus quadricauda immobilized Ca-alginate beads	Zn(II)	55.2	5.0	25	(Bayramoğlu & Yakup Arıca, 2009)
Scenedesmus quadricauda immobilized Ca-alginate beads	Ni(II)	30.4	5.0	25	(Bayramoğlu & Yakup Arıca, 2009)
SA-polyaniline nanofibers	Cr(VI)	73.34	4.2	30	(Karthik & Meenakshi, 2015)
SA-polyaniline nanofibers	Cr(VI)	74.46	4.2	40	(Karthik & Meenakshi, 2015)
SA-polyaniline nanofibers	Cr(VI)	75.82	4.2	50	(Karthik & Meenakshi, 2015)
Ca-alginate immobilized sericite bead	Ni(II)	10.743	7.5		(Jeon & Cha, 2015)
Goethite impregnated calcium alginate beads	As(V)	30.44	5.0	25	(Basu, Singhal, Pimple, & Reddy, 2015)
Phosphate-embedded calcium alginate beads	Pb(II)	263.16	4.0	25	(Wang, Yao, et al., 2016)
Phosphate-embedded calcium alginate beads	Cd(II)	82.64	5.5	25	(Wang, Yao, et al., 2016)
SA-graft-poly(methyl methacrylate) beads	Pb(II)	526	—	—	(Salisu, Sanagi, Abu Naim, Wan Ibrahim, & Abd Karim, 2016)
Alginate graft polyacrylonitrile beads	Pb(II)	454	—	—	(Salisu, Sanagi, Abu Naim, Abd Karim, et al., 2016)
SA–carboxymethyl cellulose gel beads	Pb(II)	1727	5.0	37	(Ren et al., 2016)
Quercetin loaded nanoparticles based on alginate	Pb(II)	140.37	7.0	25	(Qi, Jiang, Cui, Zhao, & Zhou, 2015)
Functional CNTs-SA	U(II)	6.01	6.0	Ambient T	(Allaboun, Fares, & Abu Al-Rub, 2016)
CNTs/CA	Cu(II)	84.88	5.0	20	(Li et al., 2010)

pronounced differences between sorption capacities of the alginate beads for different metals examined, with a general order of Pb(II) > Cu(II) > Cd(II) (Papageorgiou et al., 2006). Alginate gel beads showed a high affinity for heavy metal ions of Cu(II) and Mn(II), especially in a low concentration region. After covalently cross-linked with 1,6-diaminohexane bridges, the matrix of alginate gel beads was expected to improve the mechanical strength and resistance to chemical and microbial degradation of the beads, without the change in adsorption property. Ca-alginate beads also were applied to remove U(VI) ions from the solution and the results indicated that the interaction between uranium ions and Ca-alginate beads is endothermic in nature. Values of entropy and Gibbs free energy change

suggested that the adsorption of uranium on Ca-alginate is a spontaneous process (Gok & Aytas, 2009). That is, the covalently cross-linked alginate gel beads are expected to be a good candidate for adsorbents to remove heavy metal ions from low heavy metal concentration wastewater (Gotoh, Matsushima, & Kikuchi, 2004a).

3.2.2. Activated carbon/Ca-alginate beads

While AC has used widely to remove organic substances, AC immobilized in alginate beads has been studied for the removal of heavy metals in water and wastewater (Hassan, Abdel-Mohsen, & Elhadidy, 2014). Hassan et al. investigated three different adsorbent materials namely; KOH-activated carbon-based apricot stone (C), calcium alginate beads (G) and calcium alginate/activated carbon composite beads (GC) for the As removal. The results indicated that GC exhibited the maximum As(V) adsorption (66.7 mg g^{-1} at 30 °C) (Hassan, Abdel-Mohsen, & Elhadidy, 2014). Kim et al. studied adsorption equilibrium characteristics of Cu and phenol onto powdered AC, alginate bead and alginate-activated carbon (AAC) bead. The adsorption capacity of Cu(II) onto different adsorbents was in the following order: alginate bead > AAC bead > AC; that of phenol was: AC > AAC bead > alginate bead (Kim, Jin, Park, Kim, & Cho, 2008). Choi et al. produced a novel alginate complex by impregnating synthetic zeolite and powdered activated carbon (PAC) into alginate gel bead and found that the composite could simultaneously remove zinc and toluene from aqueous solution. The maximum adsorption capacity of alginate complex for zinc and toluene obtained from Langmuir adsorption isotherm was 4.3 g kg^{-1} and 13.0 g kg^{-1}, respectively (Choi, Yang, Kim, & Lee, 2009).

3.2.3. Biochar/Ca-alginate composites

Previous studies have indicated that engineered biochar serves as a low-cost AC alternative for adsorption of heavy metals (Ding, Hu, Wan, Wang, & Gao, 2016; Lyu, Gao, He, Zimmerman, Ding, Huang, et al., 2018; Wan et al., 2016; Wan, Wu, He, Zhou, Wang, Bin, & Chen 2017; Wang, Lee, Lehmann, & Gao, 2018). Adsorption of Cd(II) by biochar-alginate bead was studied using batch systems and continuous fixed bed columns and the results indicated that biochar-alginate beads, *Ambrosia trifida* L. var. Trifida biochar-alginate beads (ATLB-AB) can be applied as an eco-friendly and potential adsorbent for the removal of Cd(II) from groundwaters (Roh et al., 2015; Wang et al., 2018b). Do and Lee also synthesized a biochar-alginate capsule to remove lead ions Pb(II) from an aqueous solution. The maximum adsorption capacity for Pb(II) was found to be 263.158 mg g^{-1} at pH of 5.0 (Do & Lee, 2013).

3.2.4. Graphene oxide/Ca-alginate beads

In the last decade, GO has been studied for the removal of heavy metals, synthetic dyes, and other organic compounds (Bai et al., 2016; Chen, Gao, & Li, 2014; Chen et al., 2015; Zhang, Gao, Cao, & Yang, 2013). However, regeneration and separation of GO from aqueous media are difficult because it disperses so well in water. To solve this problem, several attempts were made to couple magnetic nanoparticles with fabrication of GO composites (Chandra et al., 2010; Liu, Gao, Fang, Wang, & Cao, 2016; Shen et al., 2010; Zhang, Gao, Li, Zhang, & Hardin, 2013; Zhang, Gao, Yao, Xue, & Inyang, 2012). Vu et al. fabricated magnetite GO encapsulated in calcium alginate beads (mGO/beads) to absorb Cr(VI) and As(V) from wastewater (Vu et al., 2017). They found that the mGO/bead maintained its activity in wastewater and exhibited greater adsorption efficiency for both Cr(VI) and As(V) than activated carbon and carbon nanotube. Lv et al. introduced graphene oxide (GO) into alginate gel before mixing with zero-valent iron nanoparticles (Fe_0 NPs) to create Fe_0 NPs embedded graphene oxide alginate beads (Fe@GOA beads), which were further reduced to Fe_0 NPs embedded reduced graphene oxide-alginate beads (Fe@GA beads) (Lv et al., 2017). The Fe@GA beads were examined for Cr(VI) removal. The result showed that 1% of alginate and 1.5-2.0% of Fe_0 by weight performed the best with a maximum adsorption capacity of about 34 mg g^{-1}.

3.2.5. Carbon nanotubes (CNTs)/Ca-alginate beads

CNTs-alginate beads show synergistic effects on removal of heavy metals (Wang, Gao, Zimmerman, & Lee, 2018). Studies have shown that the introduction of carbon nanotubes into alginate can improve the physicochemical properties of alginate-based composites, thereby enhancing its ability to adsorb heavy metals (Wang, Gao, Zimmerman, & Lee, 2018). Li et al. mixed CNTs and SA and added to the $CaCl_2$ solution to prepare CNTs-CA composites. The results show that the specific surface area and pore size of CA gel is 28 m^2 g^{-1} and 0.06 cm^3 g^{-1}, respectively. When combined with CNTs, the high specific surface area and pore size of CNTs can form microchannels in the composites. The specific surface area and pore size of CNTs-CA composites were 76 m^2 g^{-1} and 0.37 cm^3 g^{-1}, respectively. Under the same conditions, the adsorption capacity of Cu (II) on CA gel was better than that of CNTs. When the equilibrium concentration was 5 mg L^{-1}, the adsorption capacity was 52.1mg g^{-1} for CA gel and increased to 67.9 mg g^{-1} for CNTs-CA (Li et al., 2010). Under the same conditions, the adsorption performance of CNTs-CA composites to Cu(II) was significantly higher than that of CNTs.

3.2.6. Other alginate nanocomposites

Alginate nanocomposites have excellent functional properties, biocompatibility and special nano-effects for heavy metal remediation. Googerdchian et al. prepared the natural hydroxyapatite nanoparticles by mechanical activation method, and then compounded the particles with sodium alginate to prepare the granular and film SA/nano-hydroxyapatite composites for adsorption of Pb(II). The SA/nanohydroxyapatite composite membrane exhibited strong Pb(II) adsorption ability (Googerdchian, Moheb, & Emadi, 2012). Soltani et al. entrapped silica nanopowders within calcium alginate and reported that an optimal initial pH of 5.0 was good for Pb(II) adsorption with the maximum adsorption capacity of 83.33 mg g^{-1} (Soltani, Khorramabadi, Khataee, & Jorfi, 2014). The potential of Hal/alginate nanocomposite beads for the removal of Pb(II) in aqueous solutions was investigated, and the Hal/alginate beads removed Pb(II) through ion exchange with Ca(II) followed by coordination with carboxylate groups of alginate, in addition to physisorption on Hal nanotubes (Chiew et al., 2016). Wang, Zhang, Wang, Zhang, and Liu (2014) examined the adsorption behavior of Cu(II) onto the halloysite nanotube-alginate hybrid bead by a continuous fixed bed column adsorption experiment and demonstrated that the adsorption capacity reached 74.13 mg g^{-1}. Lazaridis et al. developed a composite alginate-goethite sorbent material for the removal of trivalent and hexavalent chromium ions from binary aqueous solutions. The sorption capacities for Cr(VI) and Cr(III) increased from 20.5 to 29.5 mg g^{-1} and 20.7 to 25.3 mg g^{-1}, respectively, when temperature increased from 20 to 60 °C (Lazaridis & Charalambous, 2005).

3.2.7. Magnetic alginate beads

Several reports documented that magnetic materials fabricated in alginate had excellent performance for the removal of Co(II), Pb(II), Ni(II), Cu(II), Cr(VI), Au(III) (Bakr, Moustafa, Khalil, Yehia, & Motawea, 2015; Bée, Talbot, Abramson, & Dupuis, 2011; Gopalakannan & Viswanathan, 2015). Bée et al. developed a magsorbent by encapsulation of magnetic functionalized nanoparticles in calcium-alginate beads and reported that it was easily collected from aqueous media by using an external magnetic field. The authors concluded that magnetic alginate beads could be efficiently used to remove heavy metals in a water treatment process (Bée et al., 2011). Synthesis of magnetic alginate hybrid beads was also tested for efficient removal of chromium (VI) (Gopalakannan & Viswanathan, 2015). The removal of nickel ions from aqueous solution using magnetic alginate microcapsules was studied and the result indicated that the sorption capacity of nickel increases with increasing pH (Ngomsik, Bee, Siaugue, Cabuil, & Cote, 2006). Metal uptake capacity at low pH is attributed to an

ionic exchange between protons and nickel ions. At higher pH, the adsorption of Ni is pH-dependent and corresponds to a competition between nickel and calcium ions. A new calcium-alginate magnetic sorbent was prepared by an electrostatic extrusion technique with a maximum adsorption capacities of arsenic and copper ions of 6.75 and 60.24 mg g^{-1}, respectively, much higher than those of commercial adsorbents (Lim & Chen, 2007). The introduction of magnetic properties into calcium-alginate beads system combines the high adsorption capacity of calcium-alginate beads and the separation convenience of magnetic materials, offering a viable technique for future applications.

3.2.8. Microorganisms immobilized in Ca-alginate beads

Alginate can be used as an immobilizing carrier to maintain the biological activity of microorganisms and enzymes for the removal of heavy metal ions. A large number of studies have shown that microbial immobilization is effective for treatment of wastewaters with low concentrations of heavy metals to meet discharge standards. Natural polymers, such as cellulose derivatives, alginate, chitosan, and chitin have been used as the matrix for immobilization of microbial cells. These polymers are also known to bind metal ions (Zargar, Asghari, & Dashti, 2015). Arica et al. used calcium alginate to immobilize white rot fungi to adsorb different metal ions in wastewater. The maximum experimental biosorption capacities for entrapped live and dead fungal mycelia of *T. versicolor* were 102.3 mg g^{-1} and 120.6 mg g^{-1}, respectively (Arıca, Kaçar, & Genç, 2001). Then Arica et al. immobilized the basidio spores of *Phanerochaete chryosporium* in alginate gel beads to remove Pb(II) and Zn(II) ions from artificial wastewater. The results indicated that the maximum biosorption capacity of alginate beads and both immobilized live and heat inactivated fungus were 230, 282 and 355 mg for Pb(II) and 30, 37 and 48 mg for Zn(II) per gram of dry biosorbents, respectively (Yakup Arıca, Arpa, Ergene, Bayramoğlu, & Genç, 2003). Ariea et al. also immobilized *Funalia trogii* biomass in Ca-alginate gel beads to adsorb Hg(II), Cd(II) and Zn(II) ions. The results indicated that the metal biosorption capacities of the heat-inactivated immobilized *F. trogii* for Hg(II), Cd(II) and Zn(II) were 403.2, 191.6, and 54.0 mg g^{-1}, respectively, while Hg(II), Cd(II) and Zn(II) biosorption capacities of the immobilized live form were 333.0, 164.8 and 42.1 mg g^{-1}, respectively (Arıca et al., 2001).

Bayramoglu et al. entrapped a white rot fungus species (*Lentinus sajor-caju*) biomass into alginate gel via a liquid curing method in the presence of Ca(II) to remove Cd(II) in a batch system. The maximum experimental biosorption capacities for entrapped live and dead fungal mycelia of *L. sajur-caju* were found to be 104.8 and 123.5 mg g^{-1}, respectively. The

Table 3. Alginate-based composites for the removal of antibiotics from aqueous solution.

Adsorbent	Adsorbate	Adsorption capacity (mg g^{-1})	pH	Temperature (°C)	Ref.
EPCs@CMCS gel beads	Tetracycline	136.9	6.0	25	(He et al., 2016)
CMCS gel beads	Tetracycline	9.47	6.0	25	(He et al., 2016)
SA/graphene oxide beads	Ciprofloxacin	86.12	—	25	(Fei et al., 2016)
GO/CA fibers	Ciprofloxacin	39.06	5.9	Room T	(Wu et al., 2013)
GO/CA fibers	Tetracycline	131.6	6.0	25	(Zhu et al., 2018)
Alginate/graphene double network hydrogel	Tetracycline	290.70	8.0	25	(Zhuang et al., 2017)
Alginate/graphene double network hydrogel	Ciprofloxacin	344.83	8.0	25	(Zhuang et al., 2017)

kinetics of cadmium biosorption were fast, with approximately 85% of biosorption taking place within 30 min (Bayramoglu, Denizli, Bektas, & Yakup Arica, 2002). Kacar et al. immobilized basidiospores of *Phanerochaete chryosporium* into Ca-alginate beads via entrapment, and the beads incubated for vegetation at 30 °C for 5 days. The alginate beads and both entrapped live and heat inactivated fungal mycelia of *P. chryosporium* were used for the removal of Hg(II) and Cd(II) ions from aqueous solution in the concentrations range of 30-500 mg L^{-1}. The adsorption capacities of the immobilized live and heat inactivated fungal biomass reached 66.1 and 112.6 mg g^{-1} for mercury and 50.0 and 85.4 mg g^{-1} for cadmium, respectively (Kaçar et al., 2002).

A large body of evidence shows that algae can effectively absorb and enrich heavy metals in sewage (Prakasham, Merrie, Sheela, Saswathi, & Ramakrishna, 1999; Rangsayatorn, Pokethitiyook, Upatham, & Lanza, 2004). The enrichment factor can reach several thousand times with an enrichment capacity up to 10% of its dry weight. Immobilization can increase the resistance of algal cells to heavy metal toxicity. Some scholars studied the removal rate of the immobilization system and compared heavy metal adsorption with dead and live algae. Prakasham et al. indicated that immobilized microbial on sodium alginate effectively removed hexavalent chromium at pH =2. The adsorbed metal ions can be desorbed by dilute sulfuric acid (Prakasham et al., 1999). Rangsayatorn et al. studied biosorption of cadmium by immobilized *Spirulina platensis* on alginate gel and silica gel and found that the maximum biosorption capacities for alginate immobilized cells and silica immobilized cells were 70.92 and 36.63 mg g^{-1} biomass, respectively (Rangsayatorn et al., 2004).

3.3. Antibiotics

As an emerging pollutant, antibiotics pose a great threat to human health and the environment in spite of their low concentrations in the aquatic environment (Kümmerer, 2009). Traditional wastewater treatment

processes do not normally work well with most antibiotics. Therefore, alginate-based composites have been investigated as a new adsorbent to remediate antibiotic pollution (Table 3).

3.3.1. Magnetic alginate beads

There are a few reports about removal of antibiotics in water using magnetic alginate beads. Kim et al. found that nZVI-immobilized alginate beads removed trichloroethylene (TCE) from aqueous solution by >99.8% (Kim et al.). Konwar et al. prepared magnetic alginate-Fe_3O_4 hydrogel fibers using a simple laboratory micropipette and found that the magnetic alginate-Fe_3O_4 hydrogel fibers were effective in adsorption of ciprofloxacin hydrochloride, while the blank alginate hydrogel fiber did not show any significant adsorption. Anion exchange mechanism mainly controlled the adsorption of antibiotic and the formation of hydrogen bonding between the antibiotic and magnetic alginate beads can also result in the increase of adsorption capacity (Konwar, Gogoi, & Chowdhury, 2015). Such magnetic alginate-Fe_3O_4 hydrogel fibers can serve as a simple and cost-effective probe for adsorption/separation of antibiotics, with additional advantages of being easy to fabricate and having high thermal stability and mechanical strength (Konwar et al., 2015).

3.3.2. Graphene oxide/Ca-alginate beads

Wu et al. prepared a new biocomposite fibers by a wet spinning method using graphene oxide doped calcium alginate (GO/CA) (Wu et al., 2013). The comparative study indicated that the addition of GO could significantly improve the adsorption capacities of ciprofloxacin onto GO/CA fibers. The encapsulation of GO into SA made the materials more porous, provided π-π electron donor-acceptor interactions between graphene oxide and ciprofloxacin, and introduced C = O bonds into the composite (Fei, Li, Han, & Ma, 2016). Zhu et al. prepared graphene oxide/calcium alginate (GO/CA) composite fibers via a freeze-drying method using calcium chloride as a cross-linking reagent between graphene oxide and sodium alginate. The maximum tetracycline adsorption capacity of the GO/CA composite fibers predicted by the Langmuir model reached 131.6 mg g^{-1}. The mechanism of adsorption was the hydrogen bonding and π-π interaction which serve as predominant contributions to the significantly enhanced adsorption capability (Zhu, Chen, Liu, & Li, 2018). To improve the adsorption capacity of double network hydrogel, physical and chemical modifications were made on alginate/graphene double network hydrogel. The modified hydrogel featured a more porous structure and more functional groups than that before modification. The maximum adsorption capacities of

Table 4. Alginate-based composites for the removal of other pollutants from aqueous solution.

Adsorbent	Adsorbate	Adsorption capacity (mg g^{-1})	pH	Temperature (°C)	Ref.
MnO_2-alginate beads	Sr(II)	102.0	—	25	(Hong et al., 2017)
Alginate/Fe_3O_4 composite	Sr(II)	12.5	6.0	25	(Hong et al., 2016)
Calcium alginates	Yi (III)	97.087	6.0	24	(Khotimchenko et al., 2015)
Sodium alginates	Yi (III)	181.818	6.0	24	(Khotimchenko et al., 2015)
Zirconium alginate beads	Fluoride	28.05	2.0	30	(Qiusheng et al., 2015)
Hydrous ferric oxide doped alginate beads	Fluoride	8.90	7.0	Ambient T	(Sujana et al., 2013)
n-HApAlgLa Composite Beads	Fluoride	4.536		Room T	(Pandi & Viswanathan, 2015)
n-HApAlgLa Composite Beads	Fluoride	4.916		Room T	(Pandi & Viswanathan, 2015)
n-HApAlgLa Composite Beads	Fluoride	5.271		Room T	(Pandi & Viswanathan, 2015)
Iron oxide loaded CA beads	La(III)	123.5	5.0	25	(Wu et al., 2010)
Magnetic alginate beads	La(III)	250	4.0	25	(Elwakeel et al., 2017)
nZnO-entrapped alginate (alginate-nZnO) beads	H_2S	—	—	—	(Gautam, Rahman, Bezbaruah, & Borhan, 2016; Gautam et al., 2017)
nZnO-entrapped alginate (alginate-nZnO) beads	Greenhouse gases'	—	—	—	(Gautam et al., 2016; Gautam et al., 2017)
Silver nanoparticle-alginate composite beads	Disinfecting bacteria	—	—	—	(Lin et al., 2013)
Ammonium molybdophosphate–CA composite	Rb(I)	49.57	3.5–4.5	25	(Ye et al., 2009)
Ammonium molybdophosphate–CA composite	Cs(I)	91.70	3.5–4.5	25	(Ye et al., 2009)
Alginate/Iron (III) Chloride Capsules	Phosphate			20	(Siwek et al., 2016)
Electrochemically modified biochar CA beads	Phosphate	214.2	4.0	10	(Jung et al., 2017)
Electrochemically modified biochar CA beads	Phosphate	292.98	4.0	20	(Jung et al., 2017)
Electrochemically modified biochar CA beads	Phosphate	342.67	4.0	30	(Jung et al., 2017)

tetracycline and ciprofloxacin on GAD were 290.70 and 344.83 mg g^{-1}, respectively (Zhuang, Yu, Ma, & Chen, 2017).

3.4. Other environmental applications

In addition to dyes, heavy metals and antibiotics, alginate-based composites have also been used for remediation of other pollutants (Table 4). For example, MnO_2-alginate beads and alginate/Fe_3O_4 composite were used to remove Sr(II) from seawater (Hong et al., 2016; Hong et al., 2017). Removal of some rare earth elements and radionuclides from water was reported using different alginate-based composites (Elwakeel, Daher, Abd

El-Fatah, Abd El Monem, & Khalil, 2017; Khotimchenko, Kovalev, Khozhaenko, & Khotimchenko, 2015; Wu, Zhao, Zhang, Wu, & Yang, 2010; Ye et al., 2009). Besides removal of cations, alginate-based nanomaterial composites were also studied for removal of some anions in water (Pandi & Viswanathan, 2015; Qiusheng, Xiaoyan, Jin, Jing, & Xuegang, 2015; Siwek, Bartkowiak, Włodarczyk, & Sobecka, 2016; Sujana, Mishra, & Acharya, 2013). Electrochemically modified biochar calcium-alginate beads was also applied to remove phosphate under batch and continuous fixed-bed column conditions (Jung, Jeong, Choi, Ahn, & Lee, 2017). With continued research and development, alginate-based nanocomposites will be increasingly applied to various fields of environmental remediation in the future.

4. Conclusions and future perspectives

Alginate-based composites have been fabricated by encapsulating various materials, such as AC, biochar, GO, CNT, magnetic and nanomaterials, as well as microorganisms into alginate hydrogels/beads with demonstrated utility as a biosorbent for environmental application. These composites offer great potential for real world applications for the removal of dyes, heavy metals, antibiotics, and other pollutants from water and wastewater. While alginate-based composites typically exhibit enhanced physical/mechanical properties over pure alginate gels or beads, the biocompatibility of alginate coupled with new properties of the encapsulated materials often lend synergetic functionalities of the new derivatives. Among these are ease of separation and regeneration of the biosorbent for wastewater treatment, reduced environmental risk of the encapsulated materials such as nanomaterials, and optimized bioprocesses of microbial immobilization technology.

Future environmental applications of alginate-based composites, which will likely evolve considerably, require further research on the mechanisms involved in pollutant uptakes by various alginate-based composites should be emphasized. Comparative studies among the composites under controlled laboratory settings can be conducted. Another research need is to optimize existing and engineer new alginate-based composites with distinct properties and novel functionalities for targeted applications. While new techniques, such as genetic engineering will likely advance the design and creation of new composite, more effective combination of materials to improve the adsorption capacity and mechanical, chemical and thermal stability when crosslinking with alginate beads can still be explored in a systematic fashion. Although not a focus in this paper, encapsulation strategies can be directly relevant to the production of new alginate-based composites to meet different applications. Parallel to this research need is

the investigation into what chemically modifies alginate, which will benefit alginate-based composites. Because alginate contains abundant free hydroxyl and carboxyl groups distributed along the polymer chain backbone, chemical modifications of these two types of functional groups that alter the characteristics of alginate can be a future research area to fabricate new alginate-based composites for targeted environmental applications.

Most of the reported studies described in this review were conducted in a laboratory setting. Scaling up for real world applications in an uncontrolled environment requires further testing as the characteristics and mechanical/thermal stability of alginate-based composites may change. For example, the dynamic swelling of alginate-based composites in soil would be influenced by varying soil physical and chemical properties in the field. Therefore, the performance of alginate-based composites under field conditions can be explored further. Such work can also be realized in studies involving multicomponent solutions and/or complex effluents under dynamic conditions to mimic the field conditions. Potential risks associated with nanomaterials or metals in encapsulated in alginate should also be evaluated when considering applications in ambient soil and water environments.

In attempts to test alginate-based composites in large-scale applications, cost and effectiveness are the important factors to be evaluated. Because microbial treatment is potentially less harmful to the environment and more cost-effective than chemical treatment or physical removal of soil or water to an off-site location, encapsulation of microorganisms in alginate beads as a carrier will be cost effective. Investigating the further effectiveness of immobilization technology, particularly in the areas of microbial survival, binding, and transport, as well as *in-situ* bioremediation of contaminated soil or groundwater will evolve alginate based technology and make it more competitive for use in remediation applications.

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