



An updated review on boron removal from water through adsorption processes

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Abstract

Boron is an essential micronutrient that has raised much interest, given the narrow balance between its necessity and toxicity. Both natural and anthropogenic emissions of boron into water sources can eventually deteriorate water quality and endanger the ecosystem. In this review, we first present a general outline of the importance of boron, boron chemistry in water, boron contamination, and its consequences followed by the recent progress in boron removal methods based on adsorption. The adsorbents for deboronation can generally be classified based on the functional groups present; chelating groups, metal oxides, and layered double hydroxides. To comprehensively address these adsorption methods, a detailed discussion on the reaction mechanism of each system is done followed by a summary of the progress in the field during the past 5 years. Finally, some characterization techniques used in deboronation studies and suggestions for future research and applications together with possible improvements to the existing systems are presented.

Keywords Boron · Deboronation · Adsorption · Water purification · Characterization

1 Introduction

Boron (B), the fifth element in the periodic table is the only nonmetal and the most electronegative element in group IIIA. In spite of its small atomic weight, B is much scarcer in space than Hydrogen (H), Helium (He), and Carbon (C) while is widely distributed in both the hydrosphere and lithosphere of the earth [1]. Boron in nature mainly exists in the form of boric acid, borates, or boron-silicates [2]. Atmospheric presence of boron is not highly significant due to the low volatility of borates. It is estimated that the average boron content varies from 1 to 500 mg kg⁻¹ in the earth's crust and 2 to 100 mg kg⁻¹ in soil [3]. The boron concentration in the ocean, the main source of boron, ranges from 0.5 to 9.6 mg L⁻¹ [4]. In ground water, the boron concentration varies widely within the range <0.3 to >100 mg/l [5]. Concentration of boron in surface waters around the world except in areas of high natural

boron is less than 0.5 mg/l. The two factors which affect the values are (1) leaching of boron from surrounding geology to the water source and (2) nonremoval of boron from water during the conventional water treatment processes. The guideline value of boron in drinking water established by the World Health Organization is 2.4 mg-B/l, while it can vary for different countries based on the standards set by them.

Due to the rise of boron global demand in various industries and the increasing presence of boron traces in water, the water quality standards have become more stringent. This resulted in the increased interest of researchers toward the remediation of boron-spiked water during last few decades. Numerous methods have been reported for the removal of boron contaminations from water including various membrane-based technologies, adsorption, electrocoagulation, and chemical precipitation. The main objective of this review is to present an insight into the significance of boron and recent advances in the research and development of adsorption-based materials for deboronation of aqueous solutions. Each method is systematically explained by including the reaction mechanism followed by reported systems within the past few years. Finally, the existing challenges in this field, the scope, and opportunities of developing new materials and systems with enhanced properties are also discussed.

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1.1 Importance of Boron

Boron is an essential micronutrient for plant growth and development and is thus an important component in food sustainability and the fight against global warming. The concentration of boron in agricultural lands and irrigation water plays a role in crop yields and the techniques used. In plants, boron is an essential component of the cell wall and affects cell wall structural integrity and stability [6, 7]. The role of B in plant metabolism is mainly associated with the ability of B to form diester bridges between *cis*-hydroxyl-containing molecules thereby causing the stabilization of molecules and *cis*-diol [8]. Boron deficiency in plants results in damaged embryos and malformed fruits, kills growing meristems, inhibit flower development, affects cell wall synthesis and lignification, and so on. In animals, dietary boron plays an important role in embryo development, bone metabolism, and immunity development [9, 10]. For humans, the reported mean B intake for men is 1.17 mg/B and for women is 0.96 mg/B [11, 12]. The safe range for B intake in human falls in the range 1 to 13 mg/day, which is mostly covered by a proper diet including nuts, dry fruits, and wine. Boron is also a very significant component in various industries including glass, semiconductors, cosmetics, nuclear reactors, and radiation treatment [13, 14].

1.2 Sources of boron contamination

Approximately 90% of boron pollution in the environment is contributed by human activity [15, 16]. Among the major sources of contribution are industries related to glass. Glass products such as borosilicate glass and insulation glass consume a significant amount of boron compounds, thereby contributing to anthropogenic boron emissions [17]. Most commercially available fire-retardant materials are also manufactured by using boron as an important additive [18]. In ceramics, borates play an important role in the manufacturing process during vitrification at low temperatures. In liquid crystal display (LCD) systems, the polarizer is made by cross-linking polyvinyl alcohol with boric acid and iodide, which is used as a dye in the process [19]. Figure 1 represents the various atmospheric and anthropogenic sources of boron contamination in water.

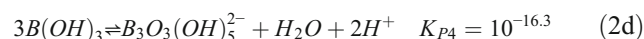
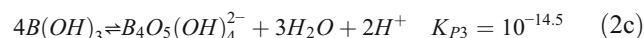
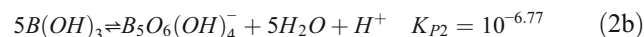
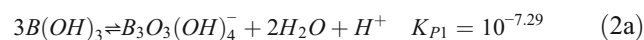
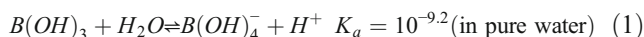
1.3 Toxicity of Boron

The difference between the concentration of boron necessary for various systems and its toxicity limit is very small. For plants, the permissible level of boron in soil for each crop is different. Exposure to excess boron in plants can cause inhibition in photosynthesis, a decrease in root development, etc., thereby affecting plant growth [26, 27]. The fatal dose of orally ingested boric acid for an adult is near the range 15–20g and for infant it is 5–6 g which is very close to the permissible level. Long-term consumption of boron-contaminated

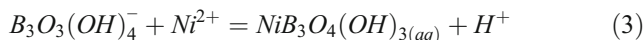
food and water by humans may cause the development of serious syndromes, persistent vomiting, diarrhea, and other cardiovascular ailments [28]. Therefore, it is significant to monitor and control the boron content in water, especially in the case of drinking water.

1.4 Boron chemistry in water

The existence of boron in an aqueous solution mainly depends on the boron concentration, pH, and temperature of the solution. Boron can be found as boric acid $B(OH)_3$ or various forms of borate ions $B(OH)_4^-$ in solution. The dominant form of inorganic boron in natural aqueous system (pure water) is boric acid which acts as weak Lewis acid in aqueous solutions and accepts hydroxyl ion to form tetrahydroborate ion in alkaline condition which is represented by Equation 1. It is reported that when the concentration of total boron is less than 0.025 M, most of the existing boron species is in the form of H_3BO_3 [29]. With a pK_a value of approximately 9.2 at 25°C, boric acid is considered a weak electrolyte and is electrically neutral [30–33]. The pK_a value indicates that at low pH (below 9), boric acid is present, and at high pH (>9) and in diluted solutions, the monoborate anion can be found. As shown in Fig. 2(a), the ratio of boric acid molecules to borate ions in aqueous solutions highly depends on the pH of the medium. These species, boric acid and monoborate, have distinct properties with the latter exhibiting an electric charge. Hence, when considering boron removal, the effectiveness of the process used depends on the type of boron species present in the feed water [34]. As the boron concentration increases, a variety of polyborate structures may form in solution (Equation 2a–2d). The tendency to form polyanionic species exists in solutions with a concentration between 0.025 and 0.6 M at a neutral to alkaline pH in the range pH 6–pH 11.

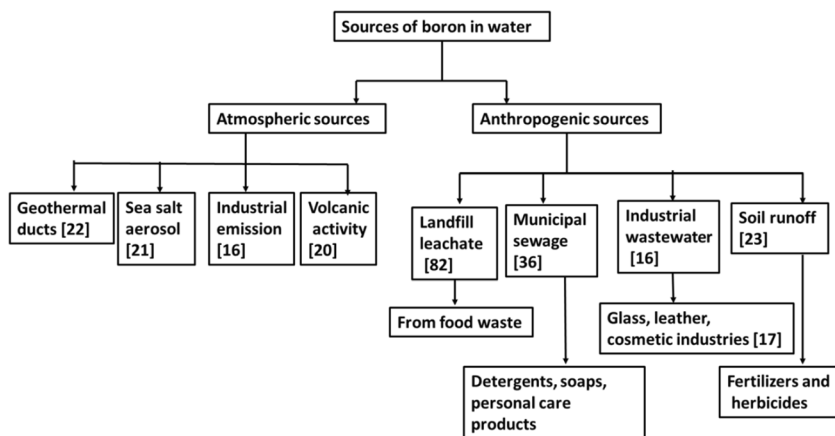


Excess borate ions present in solution can also form complexes with other metal ions present in the solution, as represented in Equation 3 [36].

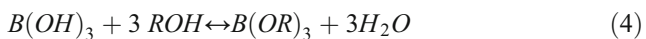


In aqueous form, boric acid and borates react with alcohols and polyols forming boron esters, *cis*-diol monoborate esters or monoborate complexes (Equation 4). This reaction results in the increase of acidity of boric acid which is the principle

Fig. 1 Various sources of boron contamination in water [16, 17, 20–25]



behind the quantitative analysis of boric acid using phenolphthalein as an indicator.



2 Boron removal technologies

Many boron removal technologies are available today. The most effective way to remove dissolved boron is by thermal desalination, which can be implemented by either multistage flash (MSF) or multi-effect distillation [37]. However, even with advanced technology, due to its high energy consumption, this approach is no longer supported by developed countries. Different approaches are being considered, each with a different level of performance and feasibility of implementation (laboratory-scale or industrial-scale approaches). All these approaches basically depend on two strategies: (i) separation by sorption on a substrate, and (ii) separation by membrane filtration. Recent studies have also focused on a hybrid approach combining sorption and membrane filtration in the same process [24, 26]. Per the Global Water Desalination

Equipment Market Report, 2020–2027, reverse osmosis technology is currently the approach most often employed for water desalination (<https://www.grandviewresearch.com/industry-analysis/water-desalination-equipment-market>).

The efficiency of the processes used has been generally evaluated considering two factors: (i) the removal ratio (R_B) of the target species (boron), and (ii) the recovery ratio (Y_W) of treated water. These factors can be calculated using Equations 5 and 6.

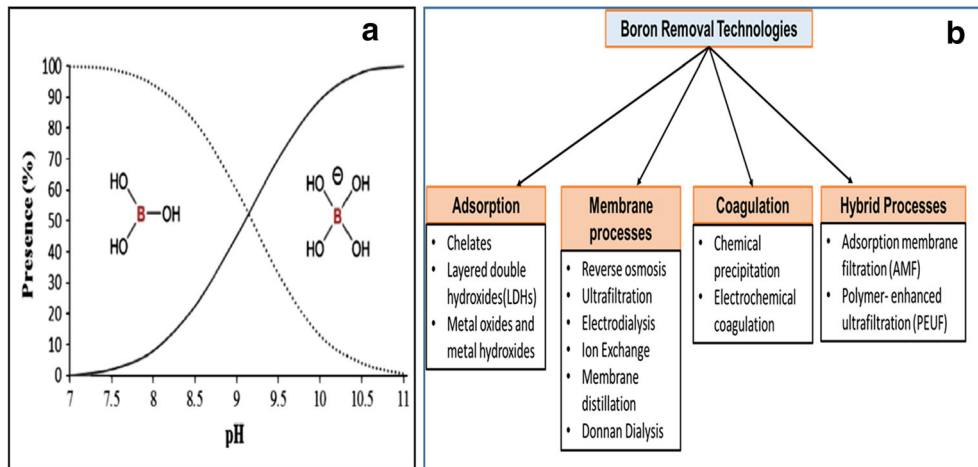
$$R_B = (C_{in} - C_{out}) / C_{in} \quad (5)$$

$$Y_W = (Q_{in} / Q_{out}) \quad (6)$$

where C_{in} and C_{out} are the concentrations of influent water (in) and effluent-treated water (out), respectively, and Q_{in} and Q_{out} are the corresponding flow rates.

The concentration of boron in water varies from place to place depending on geography, proximity to the sea, industrial areas, wetlands, etc. Considering the increasing boron concentration in various water sources and agricultural environments, current research is focusing on developing effective technologies that can be applied in various conditions according to need. Figure 2(b) represents the basic technologies available for boron removal

Fig. 2 (a) Distribution diagram of boric acid and borate ions in solution at various pH values. Adapted from [34]. (b) Various boron removal technologies



from various sources. Among the various technologies for boron removal from water, the adsorption process is most commonly used for dilute solutions, while ion exchange and membrane filtration are used for concentrated solutions. Co-precipitation of borates using metal carbonates is strongly pH dependent, while using metal hydroxides produces a large amount of sludge [38]. Adsorption and filtration are the two basic techniques involved in all technological processes involved in boron removal from water. Hybrid techniques that utilize both adsorption and membrane filtration are also in use.

3 Adsorption processes

An effective approach for boron removal from aqueous solutions with very low concentrations of boron is adsorption. The basic principle of the adsorption process is to apply various substrates or surfaces capable of adsorbing the specific species that are expected to be removed from the aqueous solutions. Depending on the material used as the adsorbent, slight changes occur regarding the overall procedure of adsorption-based filtration. Various sorbents are used in adsorption processes for boron removal, including mesoporous silica, activated carbon, clays, fly ash, natural minerals, biological materials, nanoparticles, layered double hydroxides (LDHs), selective resins, and complexing membranes. When developing an adsorbent, the main focus is on a high adsorption rate, maximum capacity, high and feasible regeneration, and low cost. Recently, researchers have become more focused on adsorbents with chelating functional groups, clays, metal oxides, carbon compounds, and natural materials.

3.1 Adsorption experiments

The general approach for adsorption experiments is demonstrated in Fig. 3. In a typical process, a fixed amount of adsorbent is added to the adsorbate solution and the mixture is stirred well at constant temperature and pH for a particular time set for the experiment. The filtrate is then collected and various characterizations are done to study the extent of adsorption. The experiment is repeated in batches to study the effect of various parameters like the temperature, contact time, pH, and concentration of the adsorbent and adsorbate on the adsorption process. pH of the solution can be varied by the addition of hydrochloric acid (HCl) or sodium hydroxide (NaOH) according to the study under consideration. The adsorbate-cladded adsorbent is systematically analyzed using various high-end techniques like X-ray photoelectron spectroscopy (XPS) to study the bonding interaction between the adsorbent and the metal pollutant. Desorption experiments for the regeneration of the adsorbent is carried out after the adsorption process and the adsorbent is again used to test the reusability of the material.

The boron adsorption mechanism is mainly defined by two steps: (i) specific affinity between the chelating group on the surface of the adsorbent and H_3BO_3 , and (ii) physical attraction driven by various forces, including van der Waals forces, electrostatic attraction (from protonated amines and $(B(OH)_4^-)$), and hydrogen bonding interactions (from $-OH$ from $H_3BO_3/(B(OH)_4^-)$ and $-OH/-NH-$ from the adsorbent). Detailed adsorption kinetic studies, isotherms, and thermodynamics of the reaction play an important role in thoroughly understanding and establishing a valid conclusion regarding the reaction mechanisms involved in the adsorption experiments [39, 40].

To analyze the parameters associated with the adsorption process, various adsorption isotherms can be used. Among them, two-parameter isotherms like Langmuir and Freundlich adsorption isotherms are frequently used due to their simplicity and easy interpretability. The Langmuir isotherm assumes a monolayer adsorption of solute on a homogenous surface and is represented by Equation 7. The Freundlich isotherm is an empirical equation based on adsorption phenomena where uptake occurs on a homogeneous surface (Equation 8).

$$\text{Langmuir model : } q_e = \frac{Q_{max}^0 K_L C_e}{1 + K_L C_e} \quad (7)$$

$$\text{Freundlich model : } q_e = K_F C_e^n \quad (8)$$

where q_e (mg/g) is the equilibrium adsorption capacity, Q_{max}^0 (mg/g) is the maximum saturated monolayer adsorption capacity of the adsorbent, C_e (mg/L) represents the solute concentration at equilibrium, k_L (L/mg) is a binding energy constant, K_F (mg/g) is the Freundlich constant, and n (dimensionless) is the Freundlich intensity parameter which indicates the surface heterogeneity.

The thermodynamic adsorption studies play a key role in defining the adsorption mechanism involved in the reaction. This study can be conducted by varying different parameters including temperature and concentration while keeping other parameters like pH and adsorbent particle size to be constant. At equilibrium, the various thermodynamic parameters of the reaction including Gibbs energy change (ΔG^0), the enthalpy change (ΔH^0), and the entropy change (ΔS^0) can be calculated using suitable equations (Equations 9 and 10). The Gibbs energy change is a significant parameter which can define the spontaneity of the adsorption process. Meanwhile, entropy change defines the arrangement of adsorbate at the adsorbent interface during the adsorption process.

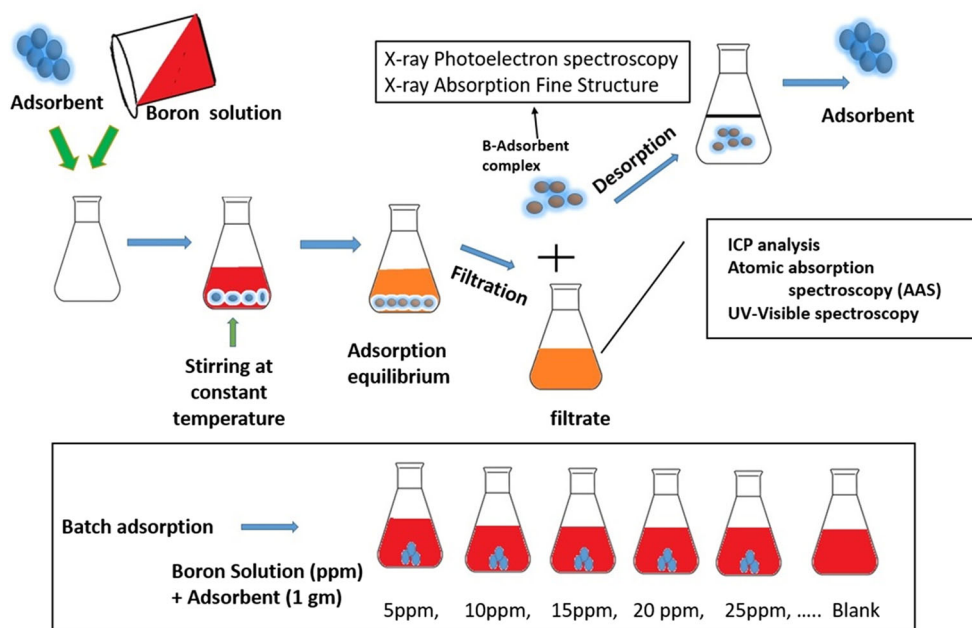
$$\Delta G^0 = -RT \ln K_c \quad (9)$$

The relationship between ΔG^0 , ΔH^0 and ΔS^0 is represented as:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (10)$$

where R is the universal gas constant ($8.314 \text{ kJ mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature (K), and K_c is a constant.

Fig. 3 Schematic representation for the general procedure of adsorption study



3.2 Chelating resins

One of the most effective and selective methods of adsorption for boron removal from aqueous solution is to employ chelating resins. Studies related to the detailed analysis of boron chemistry have shown that molecules with vicinal diols are capable of forming borate complexes with boron moieties in aqueous solutions (Fig. 4(a)) [41]. This capability indicates the possibility of designing new boron-specific adsorbents based on this chemistry. While the interaction of the diols with boron results in the formation of borates, the presence of an amine group in the chelating resin helps neutralize the effect of the positive charge formed. Hence, the presence of an amine group is also important for the efficiency and selectivity of chelating resins [42]. Chelating resins are basically polymer-supported structures with an effective boron-specific group attached to their surface. To prepare an effective and highly selective boron removal resin, different factors must be considered: (i) the strength of the polymer support, (ii) the hydrophilicity of the polymer support, and (ii) the specificity of the resin toward boron. The resin should be highly selective for boron species and have mechanical integrity, feasibility, and affordable commercial availability.

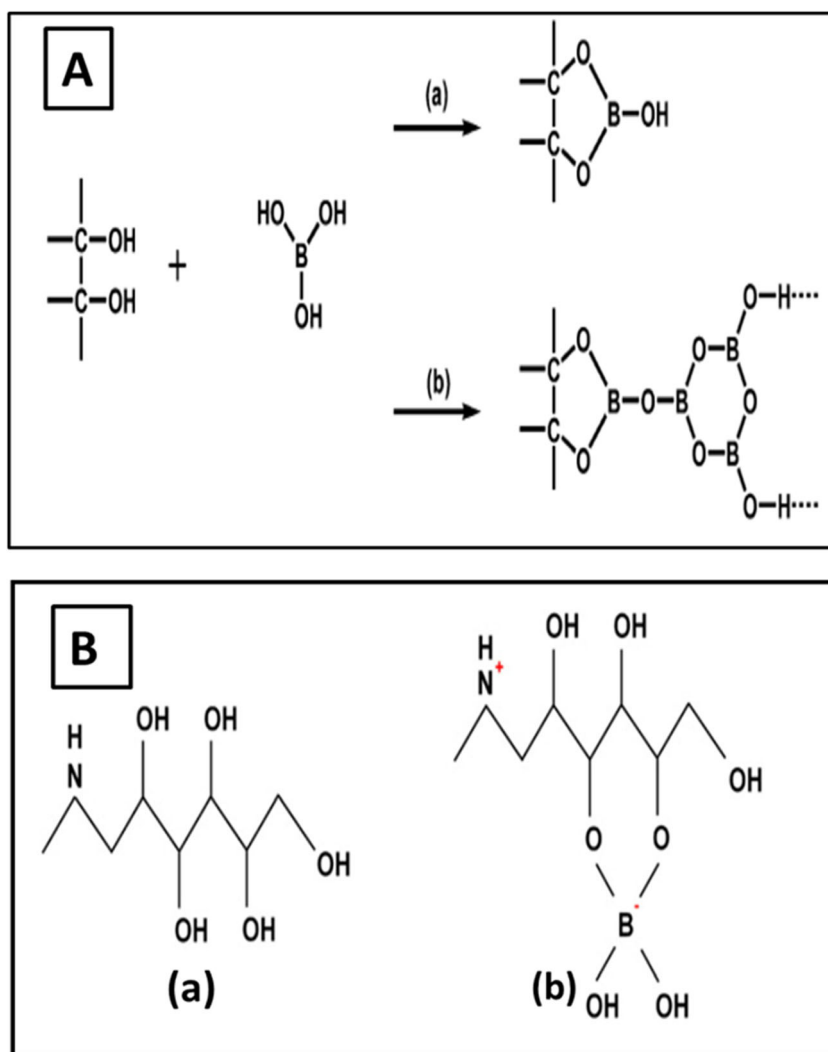
Polymers with polyhydroxyl groups, such as sorbitol [43], mannitol [44], and N-methyl-D-glucamine (NMDG), have been widely studied as boron adsorbents. Among compounds with hydroxyl groups, for a given amount of substance, D-sorbitol and D-mannitol have more hydroxyl groups than their counterparts. Hence, they can more effectively form complexes with boron. NMDG, with polyols and tertiary amine ends, is the most studied functional group for boron removal. Most available commercial boron-selective resins (BSRs),

including Amberlite PWA10, LSC 780, Diaion CBR05, and Purolite S108, are modified using this NMDG functional group. BSRs have a maximum capacity between 0.7 and 0.95 eq/L, equivalent to an adsorption capacity of 5.9–7.2 mg-B/g [45].

Researchers have extensively explored the possibilities of NMDG using various polymer supports and polymers with vicinal diol groups. The structure of NMDG and its monoborate complex is given in Fig. 4(b). For a detailed understanding of boron adsorption by D-glucamine, a molecular-scale analysis using density functional theory was reported by Ide and Hirayama [46]. They reported that the most stable mono-D-glucamine species is a tridentate 2,3,5-isomer with a free energy value of $\Delta G = -101.73 \text{ kJ mol}^{-1}$ among 30 possible configurations. The chelation mechanism between boric acid and NMDG prevents any further interaction of other cations in the specific adsorption process. It is also reported that monochelates of boric acid and NMDG are more stable than *bis*-chelates owing to their configurational stability; these types of chelates contribute 83% and 17% of adsorbed boron, respectively [47].

Initially, the main polymer used for the polymer support base was polystyrene. Because polystyrene is an anion exchange resin with a hydrophobic polymer structure that is not supportive of the mass transfer process, polystyrene-based BSRs have several drawbacks. The sorption rate with a small particle size is drastically higher than that with larger particles. However, a smaller size eventually results in clogging on the resin surface. This property has given rise to a new technology involving two techniques, adsorption followed by filtration. Another disadvantage is the low specific surface area of the resins. The number of NMDG functional groups

Fig. 4 (a) Chelation mechanisms of boric acid with diols at (a) a low boron concentration (<220 ppm) and (b) a high concentration (>220 ppm) where $B_4O_4(OH)_4$ is formed. (Adapted from [41]). (b) Structural formula of N-methyl-D-glucamine (a) and monoborate complex (b)



attached is directly proportional to the active surface area of the polymer support, which determines the efficiency of the resin. Furthermore, the swelling and shrinking of adsorbent resins during boron adsorption and regeneration cycles eventually lead to a decrease in efficiency of BSRs. The quest for a better hydrophilic polymer support with high surface area and stability has attracted the attention of researchers, and many candidates have emerged, including polyacrylic acid resins. Table 1 shows a list of adsorbents with NMDG chelating groups and their performance in boron adsorption.

Li et al. reported a novel boron adsorbent fabricated by grafting NMDG onto hydrophilic silica–polyallylamine composites (SPCs) with a maximum boron load capacity of ca. 1.55 mmol g^{-1} [55]. They suggested the formation of a 1:1 tetradentate complex of H_3BO_3 with an NMDG group, as shown in Fig. 5(a). They also noticed that the maximum boron load capacity obtained in the experimental studies was higher than the theoretically calculated value of 0.79 mmol g^{-1} , suggesting the presence of other adsorbate–adsorbent interactions.

Xu et al. reported a silica-supported NMDG adsorbent (Si-MG) constructed by anchoring NMDG-modified (3-glycidioxypropyl) trimethoxysilane to a silica surface with a maximum adsorption capacity of 1.54 mmol g^{-1} [57]. Ting et al. prepared a novel boron-selective adsorbent by radiation-induced grafting of vinyl benzyl chloride onto nylon-6 fibers followed by functionalization with NMDG [58]. A spherical organic–inorganic hybrid boron-selective adsorbent with organosiloxane functionalized with NMDG functional groups was also reported [59]. The adsorbent was synthesized by an inverse suspension polymerization method based on sol–gel chemistry. The presence of Na^+ ions has a slight effect on boron adsorption, probably because Na^+ ions shield electrostatic interactions and enhance non-electrostatic interactions. However, in the case of Mg^{2+} cations, the boron adsorption capacity is significantly enhanced because of simultaneous adsorption by $Mg(OH)_2$. Jung et al. [60] reported a boron sorbent with poly(glycidyl methacrylate) chains on the surface of porous polystyrene-based beads prepared through controlled atom transfer radical polymerization

Table 1 Adsorption capacity of boron on adsorbents functionalized with the NMDG chelating groups

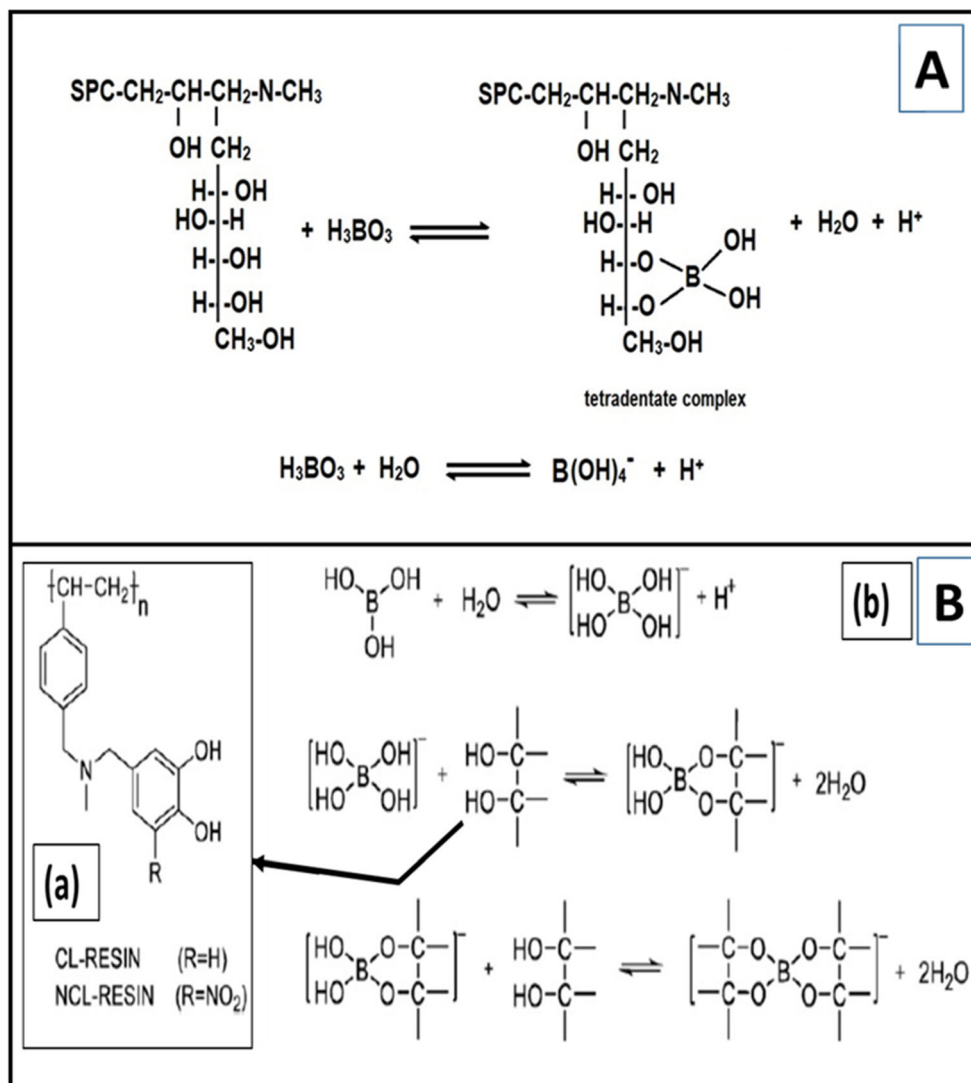
Adsorbent	Size (μm)	pH	T (°C)	KL (L/mg)	q _{max} (mg/g)	C _{e,max} (mg/L)	Regenerating agent	Reusability (cycles)	Ref
NMDG@PAF1	–	–	25	0.11	18.4	140	1 M HCl, 1 M NaOH	99% (10)	[48]
NMDG@PAF2	–	–	25	0.09	16.9	140	1 M HCl, 1 M NaOH	99% (10)	[48]
NMDG@PS-DVB	355	8.3	25	0.16	13.2	70	5% H ₂ SO ₄	99%	[49]
NMDG @cellulose fiber	175	8.3	25	0.11	18.5	70	5% H ₂ SO ₄		[49]
NMDG @cellulose spheres	100	–	25	1.65	12.4	20	–	–	[50]
NMDG@chitosan	2500	7.0	25	0.09	19.9	2000	0.5 M HCl, 0.5 M NaOH	94% (5)	[51]
NMDG@nylon fiber	30	7	30	0.11	17.2	400	–	–	[52]
NMDG@PAN nanofiber	200	7	–	–	5.5	10	0.001 M HCl	–	[53]
NMDG@aerogel	–	9.5	25	0.60	31.8	1000	3% HCl, 3% NH ₄ OH	85% (5)	[54]

*q_{max} and KL are the parameters of the Langmuir isotherm model, and C_{e,max} is the maximum equilibrium concentration of the isotherm

(ATRP), followed by reaction with boron-selective NMDG. It is notable that in this study, the boron adsorption capacity was

not linearly correlated with the grafting yield of NMDG on the polymer surface. As the length of the grafting chain increased,

Fig. 5 (a) Formation of tetradentate complex and dissociation process of boric acid. (b) (a) A pyrocatechol-modified resin and (b) suggested mechanism of boron complexation with pyrocatechol. Adapted from [56]



the pore volume decreased, resulting in a decrease in boron adsorption. Chelating resins bearing pyrocatechol functional groups can form complexes with boron in a wide pH range [61]. Figure 5(b) presents the mechanism of boron complex formation with glycol proposed by van Duin [56]. He suggested that a boron complex with glycol can be formed only at $\text{pH} > 9.07$ because of the ionization of boric acid.

Lyu et al. studied the use of pyrocatechols and nitropyrocatechol-modified resins for boron capture [62]. Optimized boron adsorption occurs at $\text{pH} 9.06$ for catechol-based resins and $\text{pH} 6.70$ for nitrocatechol-based resins, with the maximum adsorption capacities of $0.7886 \text{ mmol}\cdot\text{g}^{-1}$ and $0.7931 \text{ mmol}\cdot\text{g}^{-1}$; these values are comparable to the adsorption capacity of commercial IRA 743. Wang et al. [63] reported the synthesis of poly(amic acid)(PAA) electrospun nanofiber membranes grafted with hyperbranched polyethylenimine (H-PEI) and further with glycidol to introduce vicinal hydroxyl groups to be used for boron removal. The PAA-g-PG nanofiber membrane with a high surface area had a maximum boron uptake of 5.68 mmol/g and could adsorb 0.82 mmol/g boron from a 5 mg/L solution in 15 min with a regeneration efficiency of 93.9% after 10 cycles, indicating good regeneration of the membrane.

Multifunctional polymers based on a cyclodextrin backbone were also reported in boron adsorption studies [64]. Luo et al. [65] synthesized a β -cyclodextrin derivative functionalized with polyols to form a sponge-like osteoporotic multifunctional adsorbent that can be used to adsorb boron and organic pollutants. The boron adsorption process was found to be an exothermic process with a maximum adsorption of 31.05 mg/g .

3.3 Oxides and hydroxides

Metal oxides and metal hydroxides are capable of forming borate esters due to the presence of hydroxyl groups on their hydrated surfaces. These surface hydroxyl groups are highly sensitive to proton concentration and thus are affected by variations in pH of the boron solution. The neutral $-\text{MeOH}$ group is protonated at low pH and deprotonated at high pH . Sasaki et al. reported boron immobilization by MgO and provided the detailed mechanism involved in the reaction. When using MgO , there is a possibility for the partial hydration of MgO to $\text{Mg}(\text{OH})_2$, which can act as an active site for boron capture. They proposed the formation of the complex $\text{MgB}(\text{OH})_4^+$ during the boron removal process. Hence, compared to $\text{Mg}(\text{OH})_2$ (20%), MgO is more capable (90%) of removing boron from a solution containing 100 mg-B/L . The surface area of the metal oxides and metal hydroxides is also a key factor that influences the deboronation process. Li et al. reported the synthesis of nest-like MgO nanosheets fabricated by an ultrasonication method [66]. The mechanism of boron adsorption by MgO nanosheets is illustrated in Fig. 6.

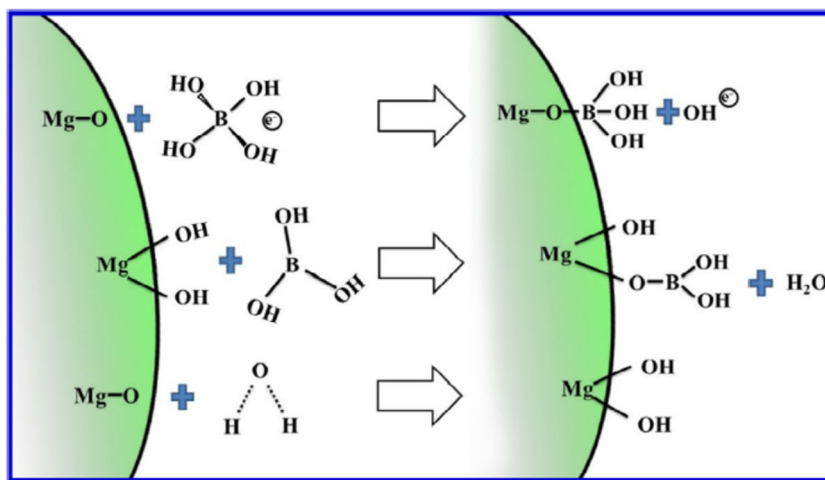
The as-synthesized MgO nanosheets possessed a higher boron adsorption capacity than the reported values for other metal oxide nanostructures. The surface area of the MgO nanosheets was enhanced to $170 \text{ m}^2 \text{ g}^{-1}$ from $80 \text{ m}^2 \text{ g}^{-1}$ for other nanostructures. During the process, tetrahedral $\text{B}(\text{OH})_4^-$ species were adsorbed onto the surface of MgO by liberating surface hydroxyls from H-bonding, and trigonal $\text{B}(\text{OH})_3^0$ was directly adsorbed onto oxygen on the MgO surface. Fukuda et al. reported a method to rapidly remove boron using low-crystalline MgO [67]. The low-crystalline MgO was synthesized by the low-temperature calcination of magnesium carbonate at $500\text{--}700^\circ\text{C}$, and the maximum surface area of $169 \text{ m}^2/\text{g}$ was obtained at 600°C .

3.4 Clays and layered double hydroxides (LDHs)

Clays and related double hydroxides appear to be potential adsorbents for boron removal due to their abundance in nature and low cost. However, it has been found that the boron adsorption capacities of clays with and without modification are comparatively poor. The performance of various clays in boron adsorption is shown in Table 2. Introducing various functional groups as adsorbing agents on the surface of clays can improve their boron adsorption properties. Demircivi and Saygili showed that by using hexadecyltrimethylammonium bromide (HDTMA) and gallic acid (GA) as adsorbing agents, the boron adsorption performance of vermiculite and perlite clays can be improved [69]. Figure 7(a and b) shows the mechanism of boron adsorption by HDTMA- and GA-modified perlite clay. Electrostatic interaction between the negative charge on the borate ion and the HDTMA- and GA-modified clay surface enables the immobilization of the borate anion. One of the main disadvantages of such modification is that the introduced adsorbents may result in secondary contamination, which limits the interest in this kind of study.

Layered double hydroxides (LDHs) are synthetic anionic clays having the general formula $[\text{M}_{1-x}^{2+} \text{M}_x^{3+}(\text{OH})_2] (\text{A}^{n-})_{x/n} \cdot m \text{H}_2\text{O}$, where M^{2+} is a divalent cation, M^{3+} is a trivalent cation, A^{n-} is an anion, and x is defined as $\frac{\text{M}^{3+}}{(\text{M}^{2+} + \text{M}^{3+})}$ molar ratio. They have been studied as potential adsorbents for boron due to their high affinity toward various boron(III) species. The structure of LDHs constitutes a layered interface with a basal plane made of divalent and trivalent metals together with interlayer anions [73]. When calcined at moderate temperatures, chemical dehydration of the metal hydroxide occurs, and the structure changes into a MgO type. The boron uptake of calcined LDHs (CLDHs) is higher than that of uncalcined LDHs. The boron removal mechanism of LDHs largely depends on the constituents present in their structure. Qui et al. [70] synthesized LDHs with different divalent

Fig. 6 Schematic diagram of boron adsorption and hydration of MgO. Reproduced with permission from [50]



metals and studied their borate removal mechanisms. They reported that for Mg-Al-CLDHs, boron is first removed via surface complexation and electrostatic physisorption by the hydroxyl groups of CLDHs; for Ca-Al-CLDHs, the primary mechanism involves the formation of boron-containing ettringite ($\text{Ca}_6\text{Al}_2(\text{B}(\text{OH})_4)_6(\text{OH})_{12}$); and for Zn-Al-CLDHs, which are pH sensitive, the primary mechanism is intercalation. Recently, monolayered nanosheets of Mg-Al-CLDHs with a specific surface area of $200 \text{ m}^2/\text{g}$ were prepared in a eutectic solvent using an ionothermal process. The Langmuir adsorption capacity was found to be 77.8 mg-B/g with a 16-fold increase in the pseudo-second-order kinetic constant compared to those of normal LDHs. One of the main disadvantages of LDHs is their low selectivity toward boron; the efficiency of boron removal from wastewater by LDHs is only 60%.

3.5 Magnetic core-based adsorbents

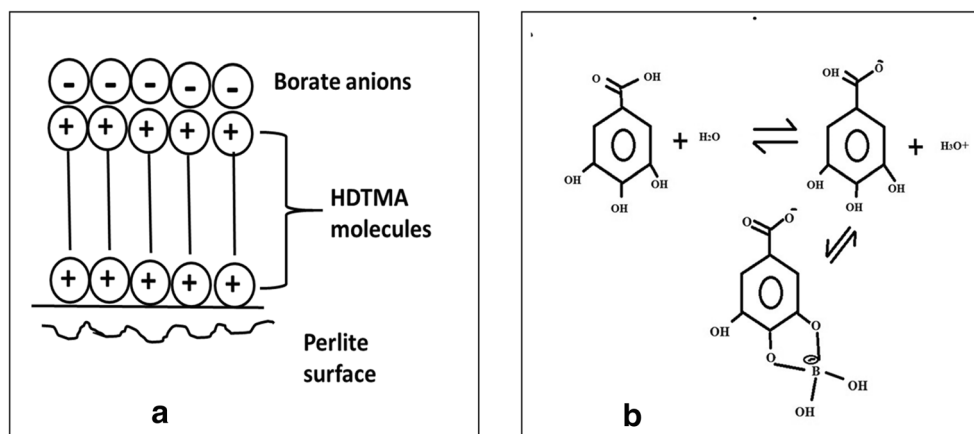
Despite being an economic and feasible process, the main drawbacks of boron removal by adsorption include the nano-scale parameters of most adsorbents, which restrict the easy recovery and regeneration of the adsorbent. To overcome this challenge, different nanosized adsorbents with magnetic cores have been synthesized for easy separation by employing a magnetic field. The most common magnetic materials involved in the design of boron adsorbents include magnetite, magnetic ferrite, and nickel ferrite. Oladipo et al. [74] first reported polyvinyl alcohol- and glycidol-functionalized MgFe_2O_4 nanopowders as boron-selective magnetic adsorbents. At 50 mg/L , the polyvinyl alcohol-functionalized particles showed lower selectivity ($S_p = 35.9\%$) and less adsorption than the glycidol-functionalized particles ($S_p = 89.5\%$), showing that the selectivity of the glycidol hydroxyl group for

Table 2 Boron adsorption performance of clay-based adsorbents

Adsorbent	q_{max} (mg/g)	K_L (L/mg)	$C_{e,\text{max}}$ (mg/L)	Ref
Bentonite	0.51	0.05	100	[68]
Kaolinite	0.60	0.05	90	[68]
Zeolite	0.53	0.04	100	[68]
Fe-Bentonite	0.83	0.03	90	[68]
Fe-Kaolinite	0.80	0.08	90	[68]
Fe-Zeolite	0.76	0.04	90	[68]
Waste calcite	1.05	0.04	80	[68]
Waste calcite-Fe	1.60	0.03	70	[68]
Vermiculite	217.4	0.31	4000	[69]
Vermiculite-GA	303.0	0.19	4000	[69]
Mg-Al-LDH nanosheets	21.6	0.006	200	[70]
Mg-Al-CLDH nanosheets	77.8	0.02	140	[70]
CQDs-LDH	20.61	0.5372	1000	[71]

* q_{max} and K_L are the parameters of the Langmuir isotherm model, and $C_{e,\text{max}}$ is the maximum equilibrium concentration of the isotherm

Fig. 7 (a) Boron adsorption on perlite using HDTMA as the adsorption agent. (b) Boron adsorption on perlite using GA as the adsorption agent. Adapted from [52]



boron is higher than that of its counterpart. Another study reported the use of magnetic chitosan-based microbeads functionalized with a glycidol group (MCG) as a selective adsorbent for boron in saline water [75, 76]. The MCG beads could be separated rapidly (within 45 s) from the test medium due to their superparamagnetic properties and exhibited repeated reusability for up to seven cycles. The MCG beads showed approximately 96% boron sorption efficiency from boric acid solution (125 mg/L) and enhanced uptake capacity (128.5 mg/g) even in the presence of competing ions and salts. In another study, a lignocellulosic magnetic hybrid (MH) was utilized for the effective removal of boron with an effective boron uptake of 108.5 mg/g at pH 7.0 [77]. An example of the mechanism of boron adsorption and removal using magnetic materials is demonstrated in Fig. 8. Here, magnetic graphene oxide (GO-Fe₃O₄) was synthesized and successfully used to remove boron from water samples.

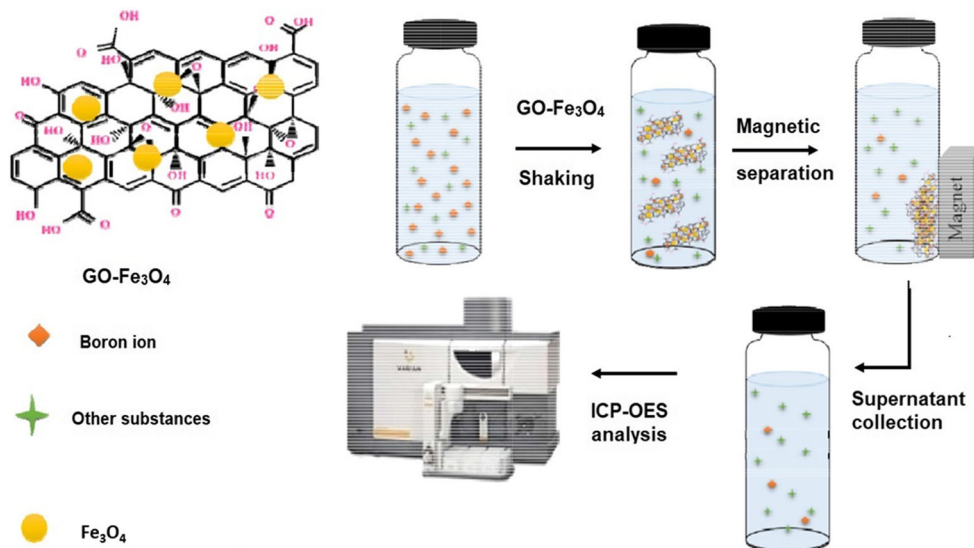
Tural et al. [79] synthesized a novel, efficient magnetic nanosorbent based on NMDG attached to magnetic nanoparticles using the click coupling method. They reported that

introducing a bulky group to crosslink silica and NMDG by cycle addition when preparing the adsorbent doubles the adsorption capacity compared to that of the product obtained through direct coupling of NMDG. Chen et al. reported the use of magnetic magnetite nanoparticles (MMNs) for the isotopic separation of boron in aqueous solution [80]. The MMNs showed a preference for ¹⁰B instead of ¹¹B, with a highest separation factor of 1.332 at pH 6, while the highest adsorption capacity (4.57 mmol/g) was found at pH 7.

3.6 Activated carbon

Activated carbon, non-graphitic carbon with high surface area and porosity, is a good adsorbent that can be used in both liquid- and gas-phase adsorption [81]. Based on their graphitizing ability, activated carbons are classified into two categories: (i) graphitizing carbons, which contain a number of graphene layers oriented parallel to each other with weak crosslinking between neighboring microcrystallites and have a relatively undeveloped porous structure; and (ii) non-

Fig. 8 Representation of boron removal using Fe₃O₄-modified graphene oxide (GO) sheets. Adapted from [78]

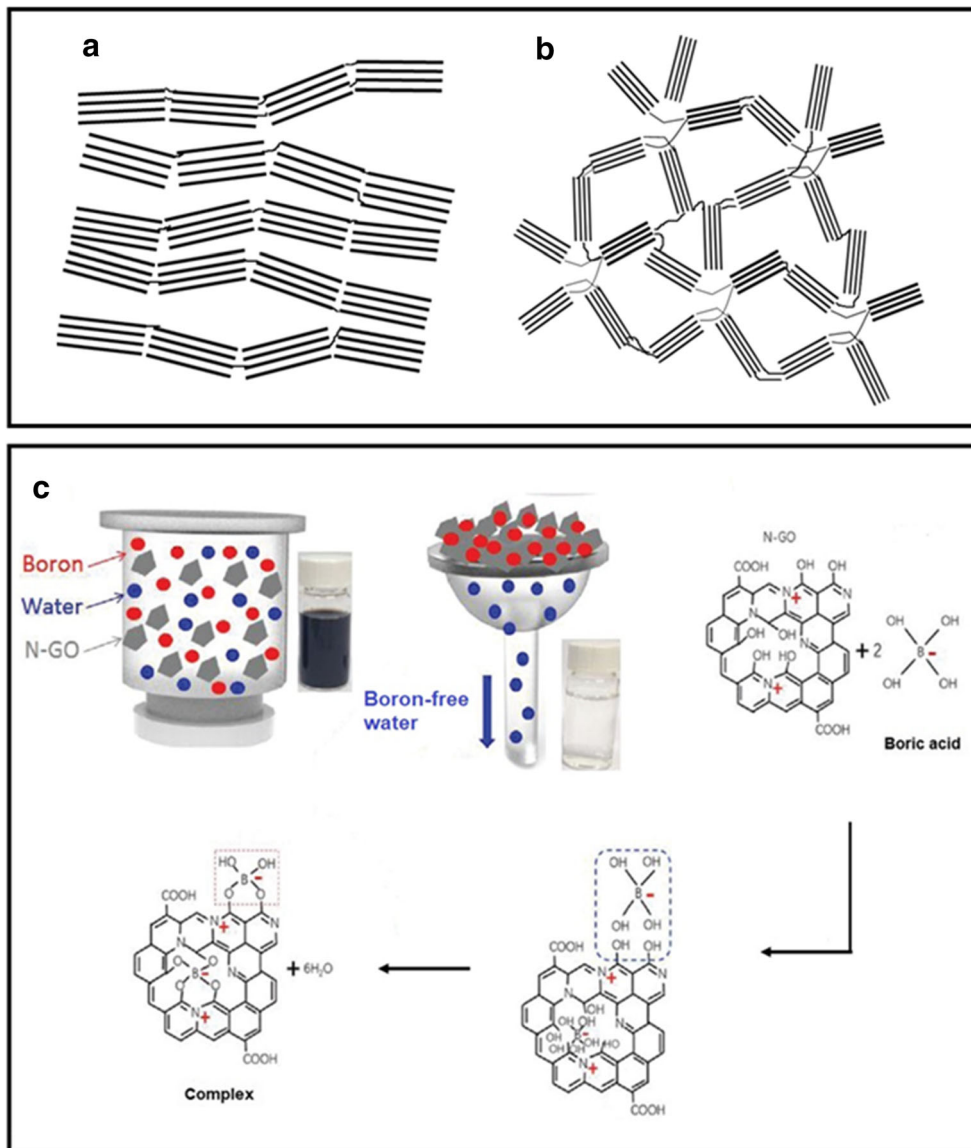


graphitizing carbons, which are hard due to strong crosslinking between crystallites and possess a well-developed micropore structure. Figure 9(a and b) shows a schematic representation of graphitizing and non-graphitizing carbons.

The main factors contributing to the boron removal capacity of activated carbon in aqueous solutions are its physico-chemical characteristics, such as surface area, pore size distribution, electrokinetic properties, and chemical structure of the carbon surface. The adsorption capacity of activated carbons is also influenced by the presence of chemically bonded heteroatoms such as oxygen and hydrogen on their surface. Electrostatic attraction is initiated between the positively charged surface of carbon and anions such as $B(OH)_4^-$, thereby forming an interaction that facilitates the process of boron adsorption.

The affinity of carbon adsorbents such as activated carbons, biochars, and carbon nanotubes toward water-soluble boron is moderate due to the presence of less surface-active boron groups on the adsorbents. To improve their boron adsorption capacity, researchers have introduced various modifications of activated carbon using various chlorides, acids, and curcumin [25, 83, 84]. Activated carbon synthesized from banana fronds was found to have a maximum monolayer adsorption capacity of 11.09 mg/g for boron from landfill leachate [85]. Kluczka et al. studied the effectiveness of various commercial activated carbons and modifications thereof for the purification of water containing dissolved boron [86]. Polyhydric chelates including mannitol, xylitol, and sodium gluconate were used for the modification, and it was found that F400 modified with mannitol showed a higher boron removal efficiency than the other investigated materials.

Fig. 9 Schematic representations of (a) graphitizing carbon and (b) non-graphitizing carbon. (c) Schematic representation of boron removal by N-GO. Adapted from [82]



Carbon-based nanomaterials such as carbon quantum dots and graphite oxide (GO) exhibit better boron adsorption properties than activated carbon. Al-Afya and Sereshti [78] studied the boron adsorption capacity of a GO/Fe₃O₄ composite prepared by introducing Fe₃O₄ nanoparticles between the GO nanosheets. The Langmuir adsorption capacity of the nanocomposite was 35.7 mg-B/L, and the interfering common ion effect was negligible. Due to the presence of magnetic nanoparticles with a saturation magnetization value of 55.8 emu/g, the separation and regeneration of GO/Fe₃O₄ was relatively effortless. In another modification of GO, Chen et al. [84] reported a new method to remove boron using nitrogen-doped graphene oxide (N-GO). Positively charged nitrogen was introduced into the intrinsically negatively charged GO sheets through a hydrothermal procedure, which fortified the electrostatic attraction toward B(OH)₄⁻. This step improved the immobilization of boron by the hydroxyl group of GO through complexation, which is shown in Fig. 9(c). It was found that the adsorption capacity of the N-doped GO was 20 times that of unmodified GO. Moreover, regeneration of the adsorbent was possible by a simple acid treatment.

3.7 Natural materials

Boron removal using waste-derived materials is highly significant considering its economic advantages. Many naturally occurring materials such as walnut shells, rice, wheat, various seeds, eggshells, and eggshell membrane (ESM) have been studied for their boron adsorption performance. Haddabi et al. [87] explored the effect of sorbent dose, contact time, and temperature on the boron removal efficiency of date palm seed ash. The boron removal efficiency of the ash was found to be 46% at neutral pH, with a minor effect of reaction time and temperature on the adsorption process. Oladipo et al. [88] reported the use of PVA-modified pomegranate seed powder for boron removal using fixed-bed column mode. The modified dose–response model was used to explain the breakthrough curve. In another study, Man et al. [89] reported the use of rice husks for boron removal with a maximum adsorption capacity of 4.23 mg/g B/L. Al-Ghouti et al. [90] investigated the use of eggshell membrane (ESM) and modified eggshell membrane (MESM) as biosorbents for boron and the effects of temperature, pH, and initial concentration on sorption efficiency. The results indicated that the adsorption of boron preferentially occurred under acidic conditions of pH 6 at 35°C, which favor a spontaneous endothermic reaction. The absorption efficiency of ESM and MESM was found to be 97% and 95%, respectively. Another study explored the possibility of using waste eggshells to remove boron from desalinated water [91].

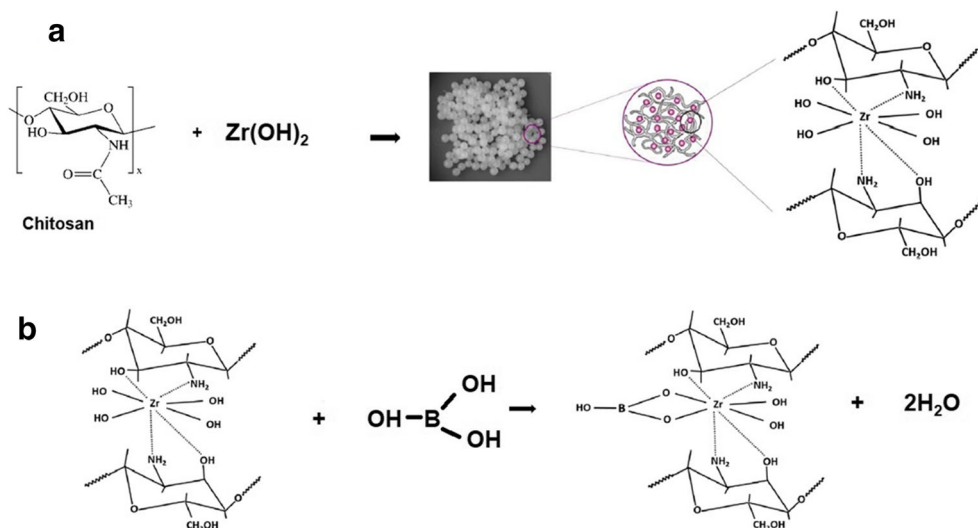
Biopolymers can be used as a matrix to anchor boron-specific functional groups due to their biocompatibility, hydrophilicity, and low cost. Tannic acid-grafted

polyethyleneimine (PEI) encapsulated in alginate hydrogel beads was used to study the efficiency of boron removal [92]. The functionalized hydrogel beads showed an adsorption capacity of 5.4 mg-B/L at pH 9. Due to the presence of amine and phenol groups in PEI and tannic acid, respectively, boron sorption at pH 12 was highly inhibited due to the electrostatic forces among these moieties. A stability and degradation study of these hydrogels showed that the adsorption capacity decreased after 2 months due to the oxidation of the phenol groups of tannic acid. Wu et al. [60] reported a more stable chitosan-based adsorbent for boron separation. Initially, the chitosan surface was modified, and 3-chlorine-2-hydroxypropyl chitosan beads (CCTs) were prepared, followed by introducing NMDG groups onto the surface to prepare a boron-specific adsorbent. The maximum adsorption capacity was 20.36 mg/g. From an initial concentration of 100 mg-B/L, the NMDG-functionalized CCTs were able to adsorb 9 mg-B/g, and there was only a 6% reduction in adsorption capacity after five adsorption–elution cycles. Duran et al. [93] reported the modification of silica hollow spheres using gum Arabic, which is a biodegradable nontoxic biopolymer. Silica was first epoxidized using epichlorohydrin as a crosslinking agent, followed by the modification of gum Arabic using the epoxidized silica hollow spheres with the ring-opening of the epoxide group. The maximum boron adsorption of the gum Arabic-modified silica spheres was reported to be 4.10 mmol g⁻¹. Recently, Kluczka et al. reported the synthesis of zirconium(IV)-chitosan (Zr-CTS) hydrogel beads for boron removal [94]. The boron adsorption process was found to be pH dependent with maximum performance at pH 6–7, and the adsorption capacity was 24.5 mg/g. Figure 10 shows the proposed mechanism for the boron adsorption process, which involves the adsorption of boron species on the surface of amorphous zirconium hydroxide through a complexation mechanism.

3.8 Porous adsorbents

Highly porous materials include mesoporous silica, zeolites, porous-organic frameworks (PAFs), and metal-organic frameworks (MOFs); owing to their high surface area, they can act as potential substrates to anchor boron-specific chelating functional groups. Polymeric resins, in general, have a low surface area and few functional groups for specific adsorption reactions. Hence, designing a MOF-polymer composite with enhanced adsorption capacity is in high demand. Wang et al. [95] reported the boron adsorption properties of an NMDG-functionalized oligomer supported on the nanocavities of the highly porous chromium-based MOF, MIL-101. The maximum functionalization of the MOF pores using NMDG was 2.23 mmol/g, which gave a high boron adsorption capacity of 24.7 mg-B/g. Even in the presence of foreign ions, there was a negligible effect on the boron adsorption capacity of the

Fig. 10 (a) Possible mechanism of interaction between Zr(IV) and chitosan. (b) Possible interaction between Zr-chitosan and B(III). Adapted from [94]



functionalized MOF composite, showing its high selectivity toward boric acid. Kamcev et al. [57] reported the modification of a porous aromatic framework (PAF) using NMDG to efficiently remove boron at low adsorbent concentrations from aqueous solutions containing highly concentrated ionic species commonly found in seawater. Notably, after modification, the surface area of PAF decreased from 4400 m²/g to 78.8 m²/g. The as-prepared PAF-NMDG had a Langmuir adsorption capacity of 18.4 mg-B/L, and boron uptake equilibrium was attained rapidly. In contrast to commercial IRA 743 (appr. 0.75 mg L⁻¹), PAF-NMDG (0.3 mg L⁻¹) was able to reduce the boron concentration to below 0.5 ppm, which is a common target of irrigation water. Nan et al. [96] reported superhydrophilic three-dimensional ordered macroporous cross-linked poly(glycidyl methacrylate) (3DOM) further functionalized with NMDG as an adsorbent for boron removal from natural seawater. The as-prepared porous organic polymer optimized with NMDG functional groups had a high adsorption capacity of 12.3 mg-B/L.

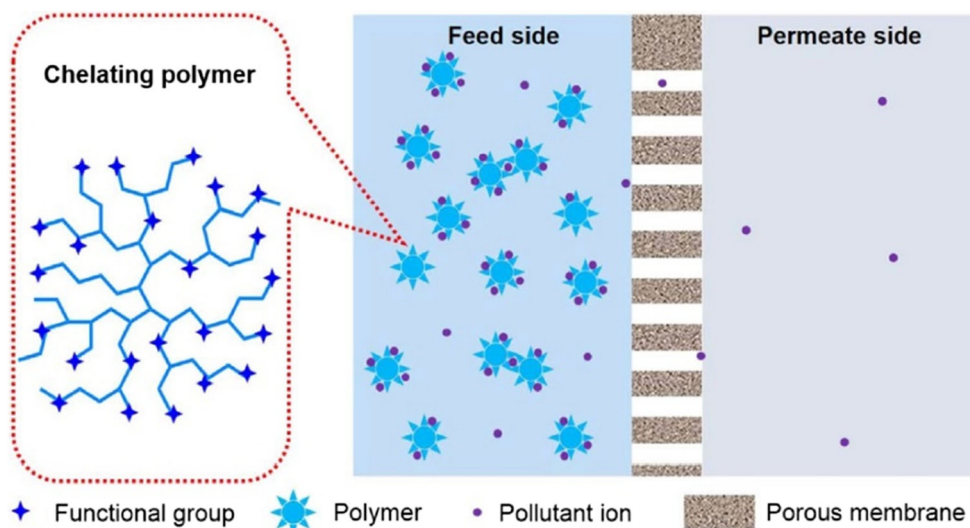
Mesoporous silica is also an ideal candidate as a highly porous substrate to anchor boron-specific functional groups. Chen et al. [97] reported the functionalization of mesoporous silica using pyrocatechol as a chelating group. At pH 9, the maximum adsorption capacity was reported to be 1.799 mmol g⁻¹ with a Langmuir adsorption capacity of 17.7 mg-B/L. Tang et al. [98] prepared diol-functionalized silica particles synthesized by grafting glycidol onto 3-aminopropyl-functionalized silica (silica-NH₂) via the epoxy-amine nucleophilic addition reaction. The as-prepared functionalized silica was able to remove 80% of the boron from an initial concentration of 11.4 mg-B/L within 3 min. Xia et al. [99] fabricated a biobased material (LS-CPAM-TA) by the electrostatic interaction-driven self-assembly of lignosulfonate, tannic acid, and cationic polyacrylamide with a mesoporous structure. The abundant catechol groups present on the surface proved to

be efficient for the removal of boron. The maximum adsorption capacity was observed to be 119.05 mg/g with excellent regeneration during recycling of the adsorbent.

4 Hybrid processes

The performance of various boron removal processes including adsorption, coagulation, sedimentation, membrane processes, and ion exchange can be enhanced by combination with two or more treatments in a single study [100]. Such hybrid techniques, by combining the efficiency of more than one separation procedure, enable a high level of water purification at a high rate. An example is an adsorption-membrane filtration hybrid process where ion exchange resins are coupled with membrane filtration for water purification [101, 102]. Cermikil et al. [103] investigated the performance of NMDG-functionalized boron-selective ion exchange resins against the commercial boron-selective Dowex XUS 43594 resin. In contrast to the boron removal capacity of Dowex XUS 43594, which is 0.52 mg/L with 95.3% efficiency, the NMDG-functionalized resin yielded 1 mg B/L after 60 min with a boron removal rate of 92%. Neo et al. [104] reported a polymer-enhanced ultrafiltration (PEUF)-based approach using novel hydroxyl-terminated polyethyleneimine (HPEI) polymers as chelating agents and polyphenylene sulfone (PPSU) as the ultrafiltration membrane for boron removal. The mechanism of PEUF is shown in Fig. 11 [105]. Synthesized HPEI-diol and HPEI-gluconamide (1000 ppm) was used to remove the boron (10 ppm) through complexation followed by ultrafiltration using a dead-end permeation cell mounted with a flat sheet PPSU membrane. HPEI-gluconamide yielded 94% boron rejection at pH 4, and HPEI-diol displayed 47% boron rejection at pH 8, demonstrating its potential for boron removal in PEUF processes.

Fig. 11 Schematic representation of the polymer-enhanced hybrid ultrafiltration (PEUF) process. Adapted from [105]



5 Boron adsorption by coagulation

Boron removal by adsorption is more efficient when the boron concentration in the source is very low. For effluent streams with a high boron concentration or with a complex constitution, coagulation approach is more efficient which transforms aqueous boron into insoluble solids. Various approaches are in use for the coagulation of boron from water including electrocoagulation (EC) and chemical coagulation. In electrocoagulation, the principle of electrochemistry is used to separate ions from water [106, 107]. This technique mainly uses aluminum and iron metals as sacrificial anodes which releases their respective cations. These cations get hydrolyzed to form their various hydroxides which in turn form surface complexes with the boron species present in the solution. Various factors including the concentration of boron, type of electrolyte and its concentration, current density (CD), and the hydraulic retention time (HRT) have impact on the removal efficiency of boron in the electrocoagulation technique [108].

Chemical precipitation/coagulation is another technique to treat the boron-containing wastewater [109]. In this method coprecipitation using calcium-based minerals or by coagulation using ferric alum or ferric chloride is followed. From a water with high concentration of boron, slaked lime recovers boron in the form of parasibirskite ($\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$) [110]. The removal of boron by this process depends on the effect of temperature, high temperature being favorable for this endothermic precipitation process. From water with a low concentration of boron, coagulation with ferric alum is a feasible approach. Boron species get chemisorbed on the surface sites of precipitated $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ [111]. It has been found that the flocs produced by the electrocoagulation exhibited better adsorption efficiency than that of chemical precipitation.

6 Characterization techniques

The role of various characterization techniques in understanding the extent and efficiency of various adsorbents in the removal of boron from solution and explaining their reaction mechanism is highly significant. Adsorption occurring at a solid–liquid interface affects the mobility of ions, thereby affecting the total charge of the solution. This charge can be monitored using an electrophoresis technique. However, the information obtained by this technique is not capable of explaining the adsorption mechanism. Therefore, more sophisticated techniques are employed to understand the adsorption process in detail. Here, a discussion on various techniques used for studying the effective boron adsorption processes from aqueous solutions is followed.

6.1 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) with surface charge measurements has been used to explain the coordination of boron on the surface of various minerals. The stretching and bending bonding interaction between the adsorbed boron species and the adsorbent surface can be deduced from the IR spectrum band shifts. Su and Suarez examined boron adsorption on various soil components, including aluminum and iron oxide, allophane, quartz, kaolinite, and calcite, at different pH values using FTIR [112]. They obtained clear evidence for the presence of trigonal and tetrahedral boron species during the study. Peak et al. reported a detailed analysis of the mechanism of boric acid adsorption on hydrous ferric oxide [113]. The mechanism of boron complexation with aluminum hydroxide was explained using spectroscopy results [114]. After boron adsorption, two new peaks appeared at approximately 1433 cm^{-1} and 1280 cm^{-1} for $\text{Al}(\text{OH})_3(\text{s})$. For boric acid solution, these peaks were distinct at 1403 cm^{-1}

and 1144 cm^{-1} . These results indicate complexation of boron on the $\text{Al}(\text{OH})_3(\text{s})$ surface, leading to the formation of strong Al–O–B bonds. Another example is 3D porous carbon quantum dot (COD)/layered double hydroxide (LDH) composite for boron adsorption from water [69]. The FTIR spectrum of the boron-adsorbed CQDs/LDHs (Fig. 12) clearly shows that the intensity of the –OH, C=O peaks of the CQDs/LDHs became weaker after adsorption of boron (III). The B–O vibration at 1413 cm^{-1} and δ B–OH vibration at 1120 cm^{-1} clearly indicated the formation of inner compounds of boron with the adsorbent.

6.2 ^{11}B -MAS NMR (magnetic angle spinning nuclear magnetic resonance) spectroscopy

^{11}B -MAS NMR was one of the main continuous wave technique used to identify the BO_3 and BO_4 units in glasses until the early 1980s [115]. This technique can also be used to explain the adsorption mechanism of boron into the solid adsorbent. The pH-dependent separation of boric acid has been extensively studied by ^{11}B NMR spectroscopy considering the fact that the ^{11}B NMR shift is directly proportional to the mole fraction of the total borate anion present [116].

6.3 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy is a quantitative surface analysis technique which uses the photoelectrons to identify the elements existing in a sample. It can also elucidate the

chemical structure and the electronic state of the elements they are bonded to. The adsorption mechanism involved in the inner-sphere complex adsorption process between the adsorbent and boron can be analyzed using XPS. Additional peak of the Adsorbent-B complex in the spectra compared to the original adsorbent corresponds to the presence of boron and also by detailed analysis it can be revealed about the kind of interaction exists between the adsorbent and adsorbate [117].

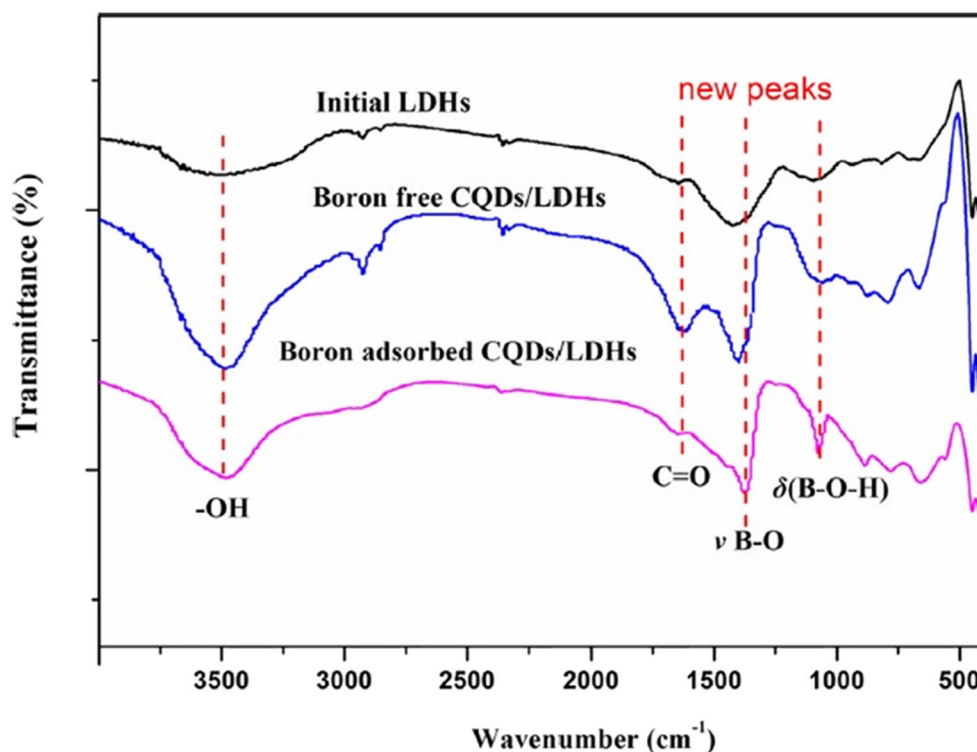
6.4 X-ray absorption fine structure spectroscopy (XAFS).

X-ray absorption fine structure spectroscopy (XAFS), is a well-known element specific technique which is highly sensitive to electronic and crystal properties [118]. Detailed information regarding the bond between atoms or electronic states of interest in a material can be extracted from the XAFS data. This technique is highly significant considering the fact that it is an element specific technique which is very important for the materials study. This study is done by analyzing the XRD results together with the XAFS measurements using certain sophisticated dedicated program software like ATHENA and ARTEMIS codes [119].

6.5 Inductively coupled plasma spectrometry (ICP)

Boron concentrations in aqueous samples are often determined by the inductively coupled plasma (ICP) methods in which samples containing boron compounds are atomized

Fig. 12 FT–IR spectra of the boron-free CQDs/LDHs and boron adsorbed on CQDs/LDHs. Adapted from [69]



into elemental B and ionized into B^+ cations. The atomized and ionized boron species are detected by the instruments using various detectors [120]. The most popular forms of ICP are inductively coupled plasma optical emission spectrometry (ICP-OES) with the standard PN-EN ISO 11885:2009 and inductively coupled plasma mass spectrometry (ICP-MS) with the standard PN-EN ISO 17294-1:2007, which can analyze a wide range of boron concentrations. Both techniques are extremely useful to detect the presence of elements at very low concentrations in the range ppb (parts per billion) to ppt (parts per trillion). In ICP-OES, an energy source of argon plasma is used to excite the electrons of the elements and those excited atoms release light at a specific wavelength as they transition to a lower energy level. By using the principle of Beer Lambert Law, the relationship between the emitted light and the concentration of elements present is analyzed by the instrument. Meanwhile, in ICP-MS, the plasma source ionizes the sample followed by the detection of these ions by an associated mass spectrum. This technique is more sensitive considering the fact that even isotopes can be detected using this method [121]. ICP-OES and ICP-MS are limited by high-salt matrix interference and the instrument detection limit. Thus, enriching the boron content and removing matrix interference are necessary before measurement.

6.6 Energy dispersive X-ray (EDX) analysis

The energy dispersive X-ray spectroscopy analysis is used for the elemental analysis of a sample. It can also give a quantitative analysis of the percentage of each element present in the sample. The presence of boron on an adsorbent after the adsorption process can be identified using EDX analysis. Due to the small atomic mass of boron, although EDX may detect boron, quantitative analysis using this technique is extremely difficult [122]. Furthermore, the presence of boron can be easily detected if it is present in the form of salts such as calcium borate by chemical precipitation using calcium hydroxide [117].

7 Problems with boron removal from water using adsorption method

The boron contamination in surface water will eventually lead to the elevation of boron concentration in drinking water source and also a life threat to aquatic ecosystem. This highlights the significance of boron remediation from water. The adsorption by chelating adsorbents for boron removal is effective to some extent. However, despite the superb adsorptive performance toward boron, many of the nanometer-sized adsorbents are difficult to separate in a large-scale operation. Adsorption also produces boron-rich brines after regeneration. Regenerability of the adsorbent is also of great concern.

Commercial boron-selective resins (BSRs) are only suitable in treating aqueous solutions with low boron concentrations up to 100 mg-B/L to avoid frequent regeneration processes and achieve a high volume contraction rate. For clay-based adsorbents, the regeneration process is uneconomic. Hence, adsorbents based on them are basically single-use, suggesting that the boron-laden adsorbents would be separated after the processes and become solid waste. Metal oxide-based adsorbents while regeneration could be dissolved in acid and base leading to the decline in their adsorption property. Hence, the reusability and integrity of the metal oxide-based composites is limited in the current reports. Characterization of boron in aqueous solutions is also challenging. Due to its small size, interference from other ionic species can occur during the analysis of boron species.

8 Conclusions and future directions

Despite the important role of boron as a micronutrient in the ecosystem for plants and animals, the emission of boron from various industrial sources to the environment endangers the ecosystem. This led to the presence of boron in various water sources which need to be treated up to the standards set by WHO and various organizations for drinking and irrigation purposes. This review summarizes the recent advances in the field of boron removal from aqueous solutions using technologies based on adsorption. The adsorbents employed in the removal of boron can be categorized into different types based on the functional groups present on them. Three main classification based on the surface active groups are chelates, clay-based materials, and metal oxide-based adsorbents. Among these adsorbents, chelating resins show promising results in boron removal studies for industrial applications. Several innovative techniques have been proposed to enhance the performance of adsorbents functionalized by chelating groups such as increasing the surface area, improving the hydrophilicity of the matrix, using magnetic constituents to improve the separation efficiency, and adding new and novel chelating groups. The orientation of hydroxyl groups in the chelates plays a crucial role in stabilizing the borate ester complex formed during the separation. Without a significant decrease in the adsorption capacity, the chelating functional groups could be regenerated several times. Despite being environmentally friendly and cost effective, clay-based adsorbents show poor selectivity toward boron, which limits their application. Metal oxides and hydroxides also immobilize boron, so novel stable metal oxide composites could be designed for deboronation. The easiness of encapsulating metal oxide structures into various biopolymers and substrates can be explored to design new novel porous materials in which the chelating functional groups are embedded on the surface. Magnetic sorbents bring together fast and efficient

regeneration during the adsorption process. Hence, the future interest lies in designing magnetic nano-sized materials with high surface area which enables fast separation after adsorption using magnetic gradient separation techniques. It is also important to develop adsorbents which can effectively function within a broad range of pH with maximum adsorption capacity.

Research interests lie in the development of efficient, durable, recyclable, and cost-effective adsorbents that can be employed in both laboratory-scale and large-scale projects for boron removal. Some suggestions for enhancing the performance of adsorbents include (i) developing adsorbents capable of boron capture at natural pH (to reduce added chemicals), (ii) increasing the boron specificity of the sorbent, (iii) developing methods for effective deboronation from concentrated solutions, and (iv) effectively regenerating the adsorbent after adsorption for reuse. Future research in this area can be improved with (i) developing new polymer supports for anchoring chelating agents to efficiently remove boron; (ii) designing new complex functional groups that can chelate with boron in a fast and efficient manner at varying pH values; (iii) developing low-cost sorbents from natural materials such as biopolymers and agricultural wastes; and (iv) developing hybrid technologies where different separation techniques can be combined with adsorption to enhance the efficiency of boron removal.

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Declarations

Conflict of interest On behalf of all authors, the corresponding author states no competing interests.

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