

CELLULOSE–BASED COMPOSITES FOR BORON REMOVAL IN SEAWATER DESALINATION: A CRITICAL REVIEW OF CHALLENGES, MECHANISMS, AND RESEARCH DIRECTIONS

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Boron removal remains a persistent limitation of seawater reverse osmosis (RO) desalination. Seawater contains 4-6 mg/L of boron, mainly as neutral boric acid, which passes through standard polyamide RO membranes, so that single pass permeate often exceeds the guideline of the World Health Organization (WHO) regarding drinking (2.4 mg/L) and irrigation limits (0.3-1.0 mg/L). Conventional solutions, consisting in a second RO pass under alkaline conditions and synthetic boron-selective resins, impose significant chemical, energy and capital costs. The review discusses cellulose-based materials as renewable alternatives for boron removal in the post-treatment stage. The extraction and adsorption-relevant properties of cellulose are outlined, and surface functionalisation strategies, particularly the grafting of N-methyl-D-glucamine (NMDG) and other polyol groups that bind boron by borate-diol ester complexation, are examined. The performance, mechanisms and regeneration of cellulose derivatives, composites and membranes are compared, and the main challenges, including selectivity at neutral pH, pilot-scale validation and techno-economic assessment, are identified as directions for future research.

Keywords: boron removal, cellulose nanocrystals (CNC), cellulose nanofibers (CNF), bacterial cellulose (BC), cellulose acetate, N-methyl-D-glucamine (NMDG), seawater desalination, reverse osmosis, adsorption mechanism, water treatment, boron toxicity

INTRODUCTION

Boron is a metalloid, displaying properties intermediate between those of metals and non-metals, and in terrestrial and aquatic environments it occurs mainly as boric acid and borate species.¹ It is considered a relatively minor constituent of the earth's crust, with an average concentration of about 8 mg/kg.³ Although it is found only in trace quantities throughout the hydrosphere and lithosphere, boron is acknowledged as a critical trace element for plant growth and development, also being vital for the health of animals and humans.² Its dual role as an essential micronutrient at trace concentrations and a phytotoxin and potential endocrine disruptor at elevated levels creates a narrow margin between beneficial and harmful effects, which complicates its management in drinking and irrigation water supplies.⁴

As global freshwater demand is projected to exceed supply by 40%, dependence on seawater desalination, which now processes over 95 million m³/day worldwide, has intensified. Yet, a persistent limitation of this technology is the inadequate removal of boron, whose unique aqueous chemistry defeats the size and charge exclusion mechanisms of standard polyamide reverse osmosis membranes.

The present review discusses cellulose-based materials as renewable alternatives for boron removal from seawater. Boron removal technologies have been addressed generically in previous reviews, which often focused on a single class of materials. Comparatively little attention has been paid to cellulose-based materials, including cellulose derivatives, cellulose composites and cellulose-based membranes, as a common platform for boron removal in the context of seawater desalination. The present review therefore summarizes the extraction methods and adsorption-relevant properties of cellulose, discusses the surface functionalisation strategies that confer it boron selectivity, compares the reported performance, mechanisms and regeneration of these materials, and identifies the challenges that must be overcome before they can be applied in desalination plants.

Boron chemistry and speciation in aqueous systems

The fundamental chemistry of boron is influenced by its small molecular size and strong affinity for oxygen.⁵ In freshwater and seawater, inorganic boron exists as neutral trigonal boric acid (B(OH)_3) below pH ~ 9.24 and as the negatively charged tetrahedral borate ion $[\text{B(OH)}_4]^-$ above this value.⁶ Boric acid acts as a weak Lewis acid in aqueous solutions, and the relative abundance of the two species is governed by the pH at low or neutral pH levels, neutral boric acid predominates, whereas higher pH favours the formation of the monovalent borate anion (B(OH)_4^-).⁷ At higher boron concentrations and rising pH values (6–10), polyborate ions, such as $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$, and $\text{B}_5\text{O}_6(\text{OH})_4^-$, can also form.^{8,9}

Boron is unusual among essential plant nutrients in that it is absorbed by plant roots mainly as the non-ionic boric acid molecule.¹⁰ Boron enters soil and water from both natural (geogenic) and human-made (anthropogenic) sources.¹¹ Geogenic sources include the weathering of rocks and soils, borosilicate minerals, such as tourmaline, volcanic activity, geothermal and groundwater sources, and seawater.¹² Anthropogenic sources arise from the extensive use of boron in industrial and consumer products, including fiberglass, borosilicate glass, cleaning products, vitreous enamels, and boron-fertilizer, as well as from wastes generated by mining and processing industries.¹³ Sodium borate is one of the commonly used chemicals for cleaning products and detergents, which contributes to boron discharge into domestic wastewater.¹⁴ The intensive use of fertilizers and irrigation methods, for maintaining good farming practices, can also lead to a rapid increase in boron levels in agricultural soils.

Environmental and health impact of boron

Boron is an essential micronutrient, but its beneficial concentration range is very limited, resulting in a narrow margin between deficiency and toxicity levels, which complicates its management.¹⁵ The excess accumulation of boron, often intensified by industrial and agricultural runoff, creates threats to ecosystems and human health.

High boron concentrations in soil and water present risks to ecological health. Although boron is vital for plant growth, for supporting cell wall formation and integrity, too much of it can be harmful, especially in plants growing in dry regions.¹⁶ High boron levels in irrigation water can cause toxicity in plants, leading to symptoms like leaf necrosis, yellowing, and lesions, which will reduce root development and crop yields.¹⁷ For animals and humans, consuming food or forage with excessive boron can cause health issues. Acute exposure to boron may result in diarrhoea, kidney damage, and even death caused by circulatory failure. Long-term exposure to boron can lead to neurological problems, kidney damage, reduced appetite, and reproductive issues.^{18,19} Animal studies have shown that high boron intake can affect male fertility, and cause low birth weight, birth defects, and developmental delays in females.²⁰

Therefore, regulatory agencies established guidelines to protect public health. The World Health Organization (WHO) established guideline values for boron in drinking water from 0.5 mg/L to 2.4 mg/L, while the Environmental Protection Agency (EPA) suggests that lifelong exposure to boron in drinking water should not exceed 1 mg/L, and considerably lower concentrations (0.3–1.0 mg/L) are recommended for the irrigation of boron sensitive crops.²² Meeting these guidelines requires targeted strategies for boron elimination.

Need for boron removal and risk mitigation

Considering the known toxic effects of boron, and that its use in industry is growing and its discharge into the environment increases, effective risk management becomes crucial.²¹ Research into cost-effective techniques, such as electrodialysis and electrocoagulation, for removing boron from polluted irrigation water is vital to addressing the main human related sources of boron from agricultural soils. Also, boron-contaminated soils and water can be remediated by physicochemical methods, such as phytoremediation, adsorption, reverse osmosis, immobilization and nanofiltration).

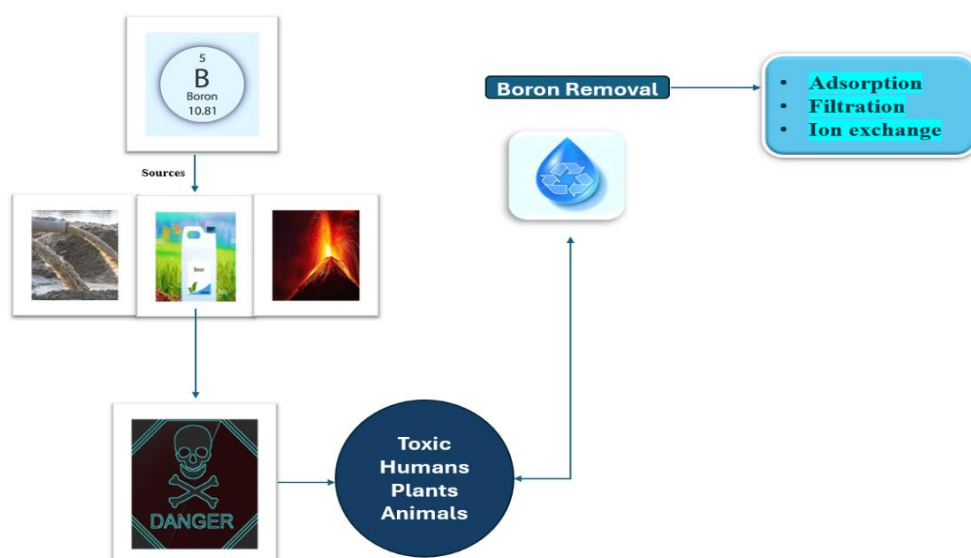


Figure 1: Sources, toxicity and removal methods of boron from water

Boron removal from water is challenging because boron exists mainly as neutral boric acid and negatively charged borates, with boric acid predominating at neutral pH, which makes it hard to remove by charge-based methods like reverse osmosis.²³ The particle size of boric acid is small, and it is highly soluble, can easily pass through membrane pores and forms hydrogen bonds that facilitate its permeation. Boron is electron deficient in nature, it forms stable complexes with polyhydroxy compounds, which complicate its interactions with adsorbents and membranes. Additionally, the concentrations of boron in water are usually low, requiring highly selective removal techniques, whereas high boron levels pose saturation problems. Moreover, boron removal processes, such as electrocoagulation, chemical precipitation, and adsorption face some operational limitations, such as sludge generation and regeneration difficulties, which reduce their cost effectiveness and efficiency. Together, these factors make boron removal from water become a complex and demanding process.

This review will proceed to describe the desalination process and its inherent drawbacks with respect to boron, in order to then focus on cellulose-based materials: the extraction methods and properties of cellulose, surface functionalisation for boron removal, the characterization of functionalized cellulose and its performance, as well as mechanisms and kinetics of the removal process. The regeneration and reusability of cellulose-based materials developed for boron removal are also discussed. The final sections outline the main challenges and future perspectives, and the conclusions drawn.

SEAWATER DESALINATION: PROCESSES AND BORON RELATED DRAWBACKS

Desalination technologies are broadly classified as thermally driven multi-stage flash (MSF), multi-effect distillation (MED), pressure driven reverse osmosis (RO), nanofiltration (NF), and electrically driven electrodialysis (ED). As of 2025, RO accounts for approximately 84% of global installed desalination capacity, driven by its lower specific energy consumption (3-5 kWh/m³) relative to thermal processes (>10 Kwh/m³) and continuous membrane innovations.²⁴ The following subsections describe the principle of desalination processes and their specific limitations with respect to boron removal, providing the essential context in which cellulose-based materials are evaluated.

Reverse osmosis: principles and boron rejection limitations

Seawater reverse osmosis (SWRO) operates by applying hydraulic pressure (55-82 bar) in excess of the osmotic pressure of seawater across a thin-film composite (TFC) polyamide membrane. Water molecules permeate the dense active layer, while dissolved solutes are preferentially rejected through a combination of size exclusion and charge repulsion.²⁵ The SWRO process as implemented at industrial scale comprises four subsystems: seawater intake and pre-treatment (coagulation, sedimentation, cartridge filtration); high pressure pumping with energy recovery devices (pressure exchangers,

isobaric chambers); the spiral wound membrane module array; and post treatment (remineralisation, disinfection, pH adjustment).²⁶

Standard polyamide TFC membranes reject 99.5-99.8% of dissolved sodium chloride, but only 60%-80% of boron at seawater pH (7.8-8.2), because neutral boric acid diffuses through the membrane through solution-diffusion transport uncoupled from electrostatic rejection.²⁷ A machine learning analysis of 11 membrane and operational variables confirmed that feed pH, membrane type, and NaCl rejection are the dominant determinants of boron rejection, underscoring the sensitivity of boron removal to operational conditions. Boron rejection improves substantially above pH 9.5, as the charged borate ion is subjected to electrostatic exclusion, enabling two-pass SWRO+BWRO systems (seawater + brackish water RO) to achieve >91% overall rejection.

Multi-stage and two-pass RO: effectiveness and economic burden

Two-pass RO, in which SWRO permeate is reprocessed through a second brackish water RO (BWRO) stage under alkaline conditions (pH 9-10) is the most widely used strategy for regulatory compliance in boron sensitive applications. However, this configuration requires the continuous dosing of sodium hydroxide (NaOH) upstream of the second pass and hydrochloric acid (HCl) for pH neutralisation of the product water, generating significant chemical waste and operational expenditure. For a 200,000 m³/day plant, alkaline dosing costs alone may reach USD 2-5 million per year, and a second RO pass increases capital cost by 30-50% relative to single-pass systems.^{28,29}

Furthermore, operating RO membranes at pH >9 accelerates membrane degradation through hydrolysis of the polyamide active layer, increases scaling propensity (CaCO₃, Mg(OH)₂), and shortens membrane lifetime, introducing additional long-term maintenance costs and operational complexity.³⁰ Selective hybridisation of multi-stage RO configuration with low pressure membranes and counter current circulation can achieve boron concentrations of ≤0.5 mg/L without bulk pH adjustment, but such configurations remain rare at commercial scale.³¹

Ion exchange resins: performance and operational constraints

Boron selective ion exchange resins (BSR) bearing N-methyl-D-glucamine (NMDG) or polyol functional groups grafted onto polystyrene-divinylbenzene matrices achieve the highest boron selectivity of any established technology, reducing effluent boron to below 0.01 mg/L for semiconductor-grade water treatment.³² SWRO+BWRO+BSR hybrid systems represent the gold standard for maximum boron removal. However, BSR systems impose recurrent chemical burdens like periodic regeneration with NaOH (boron desorption) followed by HCl (resin re-protonation), generating hazardous waste streams, and adsorption capacity drops markedly in high-salinity matrices (>1% NaCl) because of competitive ions. The petroleum derived polystyrene divinylbenzene backbone is energy-intensive to produce, non-biodegradable, and poses end-of-life disposal challenges that contrast sharply with the sustainability imperatives driving the water sector.

These limitations have motivated the exploration of bio-based alternatives, principally cellulose-based materials, capable of replicating NMDG-type selectivity with a lower environmental footprint.³³

Thermal desalination and boron behaviour

In thermal desalination processes, including MSF and MED, seawater is evaporated and the vapour is condensed to produce fresh water. However, boric acid has measurable vapour pressure and partially co-distils with water vapour, resulting in boron concentrations of approximately 0.3-1.0 mg/L in distillate, depending on operating temperature and stage configuration. Thermal processes thus only partially reduce boron and cannot, without post-treatment, reliably achieve irrigation grade water quality in regions with naturally elevated seawater boron concentration. MSF plants therefore apply additional post-treatment to achieve compliance, making boron management a multi-technology challenge even in thermal desalination.³⁴

Table 1 summarises the principal desalination and boron removal technologies and their key limitations. All established approaches need to either compromise on effluent quality, impose high chemical or energy demands, or rely on expensive post-treatment stages. This technological gap defines the opportunity space for cellulose-based materials, which make sustainable, selective, cost-competitive adsorbents and membranes that could be integrated into existing desalination treatment chains, without replacing infrastructure or requiring bulk pH adjustment.

Table 1
Comparison of principal desalination and boron removal methods

Desalination method	Principle	Boron rejection (%)	Key drawbacks	Refs.
Single-pass SWRO (polyamide)	Pressure driven membrane separation pH ~7-8	60-80% at pH 7; 91% at pH>9.5	Insufficient single pass boron rejection	35
Two-pass RO (SWRO+BWRO)	First-pass permeate re-processed under alkaline conditions	>91%	High chemical (NaOH/HCl) and energy costs Scaling risk	36
Ion exchange resin (NMDG-BSR)	Diol-borate complexation on synthetic resin beads	>99%	High capital cost Resin regeneration waste Salinity sensitive	37
Nanofiltration (NF)	Size + charge exclusion through NF membrane	~60-85%	Lower selectivity than RO Requires alkaline pH for high rejection	38
Multi-stage flash (MSF)	Thermal evaporation/condensation	~50%	High energy consumption Boron partitions into distillate	39
Electro sorption (bipolar membrane)	<i>In-situ</i> pH modulation + functionalised electrode capture	>90%	Lab scale only Electrode long-term stability unproven	40

WHY CELLULOSE? PROPERTIES AND ADVANTAGES FOR BORON REMOVAL

Cellulose has many inherent qualities that make it attractive for developing materials for environmental remediation. It is a plentiful renewable resource, with an estimated annual biomass production of approximately 1.5×10^{12} tons, making it economically sustainable.⁴¹ Cellulose is insoluble in water, which is a crucial property for filtration and adsorption applications, and its backbone carries a large number of hydroxyl groups. The hydroxyl groups on the D-glucose units allow chemical modifications, leading to a wide range of functional polymers and derivatives.^{42,43} The interactions between cellulose and borate anions are used in several areas, including engineered wood composites, textiles, fire retardants, and environmental remediation; many cellulose derivatives have been specifically designed as adsorbents for borate and phosphate.

Cellulose is the most abundant natural biopolymer. Structurally, it is a linear homopolysaccharide made up of β -D-glucopyranose units linked by β -1,4-glycosidic bonds.⁴⁴ The conversion of cellulose and other biomass-derived polymers to adsorption materials has emerged as a feasible route for sustainability, health, and environmental applications. Nowadays, cellulose can be used in wastewater treatments, in the form of adsorbents, formulated membranes, coagulation, flocculation, and antifouling agents.⁴⁵ Agricultural residues, such as date pits, pineapple crown leaves, rice straw, fruit wastes *etc.*, are frequently used as cellulose sources.⁴⁶ Microcrystalline cellulose (MCC), carboxymethyl cellulose (CMC) and nano-sized cellulose are available in commercial forms.^{47,48}

Extraction methods and properties of cellulose

For water treatment applications, cellulose is usually isolated from lignocellulosic biomass, including agricultural wastes, in which it is associated with hemicelluloses, lignin and minor non-cellulosic components.^{49,50} Isolation combines a physical pretreatment, such as grinding, milling, pulping or ultrasonication, which reduces particle size and increases the accessible surface area.^{51,52} Alkaline treatment, most often with NaOH, removes most of the hemicelluloses and part of the lignin, and a subsequent bleaching step with oxidising agents, such as sodium chlorite, hydrogen peroxide or peracetic acid, removes the residual lignin and chromophores.^{53,54} The purified cellulose can be used directly, modified or converted into nanocellulose (Fig. 2).

Nanocellulose is obtained from purified cellulose mainly by two top-down routes.⁵⁵ Cellulose nanocrystals (CNC) are produced by controlled acid hydrolysis, in which hydronium ions preferentially cleave the glycosidic bonds in the more accessible disordered regions, leaving rod-like crystalline segments.^{56,57} Sulphuric acid is the most widely used reagent due to its efficiency,

convenience and low cost. It also introduces negatively charged sulphate half-ester groups on the crystal surface, which impart colloidal stability.⁵⁸ Hydrochloric acid and phosphoric acids are the alternatives that yield nanocrystals with different surface chemistry, morphology and polymorphism.⁵⁹ Cellulose nanofibers (CNF), in contrast, are produced mainly by mechanical fibrillation, typically ending with high pressure homogenisation, and consist of long, flexible fibrils that retain both ordered and disordered domains.

Bacterial cellulose (BC) is obtained by a bottom-up route, being synthesised by bacteria as a highly pure nanofibrillar network, free of lignin and hemicelluloses.⁶⁰ Meanwhile, regenerated cellulose and cellulose esters, such as cellulose acetate (CA), obtained by dissolution or derivation, are the usual basis of cellulose membranes. Because the yield, crystallinity, dimensions and surface chemistry of the product depend strongly on the source and on the treatment conditions, the extraction route should be selected according to the intended form of the adsorbent or membrane.

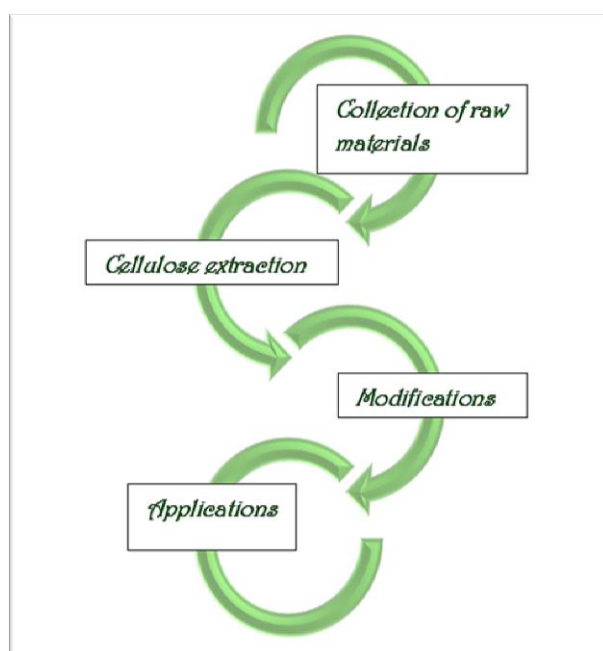


Figure 2: Graphical overview of cellulose extraction and applications

For boron removal, the most relevant properties of cellulose are the density and accessibility of its hydroxyl groups, its crystallinity, specific surface area, surface charge and physical form.⁶¹

Each anhydro glucose unit carries three hydroxyl groups (at C2, C3, and C6), but in native cellulose, most of them are engaged in intra- and intermolecular hydrogen bonds within the crystalline domains, so that mainly the hydroxyl groups located at fibril surfaces and in disordered regions are available for adsorption or chemical modification. Reducing the fibre dimensions to the nanoscale therefore greatly increases the specific surface area and the number of accessible reactive sites.

Crystallinity plays a dual role: highly crystalline materials, such as CNC, are mechanically and chemically robust and swell little, which favours their use in packed beds and membranes, whereas less ordered materials, such as regenerated cellulose, swell more in water, facilitating the diffusion of solutes towards the binding sites.

The surface charge, determined by the extraction route and by modification, controls the electrostatic interactions with borate anions, which are repelled by negatively charged surfaces, but attracted by protonated amine groups. Cellulose can also be shaped into fibers, beads, microspheres, hydrogels, aerogels and membranes, allowing the same binding chemistry to be implemented in batch, fixed bed or membrane configurations.⁶²

The intrinsic affinity of cellulose for boron is low as the boric acid forms stable cyclic esters preferentially with cis-oriented vicinal diols, whereas the secondary hydroxyl groups at C2 and C3 of the glucopyranose ring are trans-oriented and bind boron only weakly.

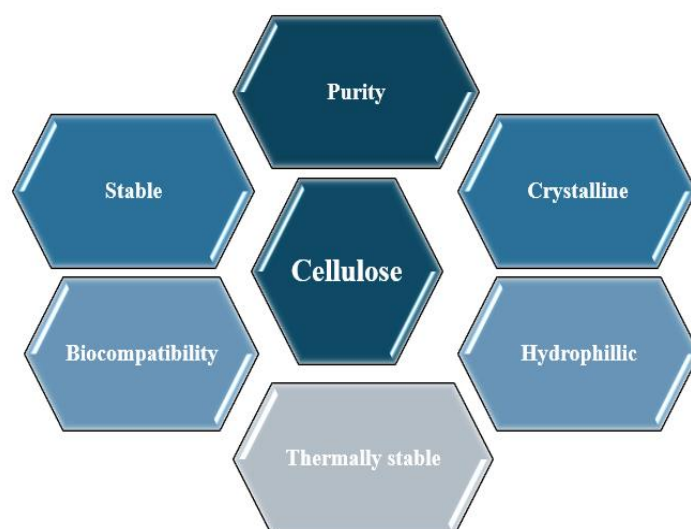


Figure 3: Characteristics of cellulose

Surface functionalisation of cellulose for boron adsorption

The intrinsic adsorption capacity of unmodified cellulose for boron is only about 1.3-3.0 mg/g.⁶³ Therefore, surface functionalisation is essential to obtain useful adsorbents. The hydroxyl groups of the anhydrous glucose units can be modified by esterification, etherification, grafting or oxidation, and the reactivity and distribution of the substituents depend on the reaction conditions.⁶⁴ Cellulose modification can be achieved by covalently attaching boron-binding groups to the cellulose backbone, resulting in N-methyl-D-glucamine (NMDG) grafted cellulose, NMDG-modified cellulose acetate or aminated nanocellulose.⁶⁵ Cellulose composites combine cellulose with a second phase, such as a synthetic polymer network, magnetic nanoparticles or a metal-organic framework, in which cellulose acts as a scaffold or co-functional component. Cellulose-based membranes use regenerated cellulose, cellulose acetate or nanocellulose as the membrane material or as a nanofiller.

Each approach addresses a different limitation of native cellulose. Modification introduces functional groups with a much higher affinity for boron than the trans-oriented C2/C3 hydroxyl groups of cellulose and allows the ligand density to be controlled. Nanocellulose (CNC, CNF and BC) offers a larger specific surface area and a higher density of accessible surface hydroxyl groups than macroscopic fibers, so that more ligands can be grafted and are more accessible to boron, for example amino-modified and amino-polyol functionalised nanocellulose reached capacity of 50-120.9 mg/g.⁶⁵ Composites are manufactured based on these advantages by introducing properties that pure cellulose cannot offer, including mechanically robust, swelling-resistant hydrogels, magnetic recoverability, molecular imprinting, and the high surface area of inorganic or framework constituents.⁶⁶ At the same time, cellulose provides a renewable, hydrophilic and biodegradable support that can be obtained from agricultural wastes, in contrast to the polystyrene-divinylbenzene matrix of commercial boron-selective resins.

The most effective and widely studied functional group for selective boron uptake is N-methyl-D-glucamine (NMDG), the same ligand used in commercial boron-selective resins.⁶⁵ NMDG consists of an open-chain polyol with five hydroxyl groups and a tertiary amine group. Boric acid, a Lewis acid, reacts with two adjacent hydroxyl groups of the ligand to form a tetrahedral borate ester. The NMDG chain is flexible, its vicinal hydroxyl groups can adopt the cis-like arrangement required for chelation. The tertiary amine is also important. It absorbs the proton released during borate ester formation, and the resulting positive charge balances the negative charge of the complex. This lets boron be captured even from near-neutral solutions. Since the binding is reversible, acid breaks the ester apart, allowing the adsorbent to be reused.

NMDG and other polyols are usually attached to cellulose through a reactive spacer. A common method is to first attach glycidyl methacrylate (GMA) to cellulose or cellulose acetate, and then react its epoxide ring with the amine group of NMDG. This approach was used to make CA@NMDG and the cellulose-based GMA-NMDG adsorbents.⁶⁵ NMDG has also been attached using radiation induced

grafting, as in the cellulose microspheres, and to other bio-based materials, such as olive tree pruning waste and wood. Other polyols, like ribose, have also been tested, but they captured less boron than NMDG. Besides polyols, researchers have added primary amines (A-NCC), branched amino-polyol structures (AP-CNC), and ionic liquids (IL-CNC@DP) to nanocellulose. These groups combine diol binding with the electrostatic attraction of borate. In every case, the grafting density sets the maximum capacity. It should therefore be reported and optimised, along with how easily boron can reach the ligands.

Characterization of functionalized cellulose: structure and morphology

The characterization of functionalized cellulose aims to confirm that the boron-binding groups have been introduced to quantify their amount, and to assess how the modification has changed the structure and morphology of the material.⁶⁷ FTIR spectroscopy tracks the chemical changes.^{68,69} When NMDG is grafted onto cellulose, new C-N bands appear and the O-H/N-H region changes, which shows that grafting worked. Weaker O-H bands, along with new bands such as the C=O band from acetyl groups, show that some hydroxyl groups have been replaced.⁷⁰ When GMA is used as a linker, the epoxide band disappears because NMDG opens the epoxide ring.⁷¹ Native cellulose contains no nitrogen, so measuring nitrogen by elemental analysis or EDX is the most direct way to find out how much NMDG or amine has been grafted. This tells you how many boron binding sites are available. TGA adds to this by showing how much of the material's weight comes from the grafted groups and how the modification affects its heat stability.⁷²

XRD shows that most chemical modifications lower the crystallinity of cellulose I. The reagents react first with the more open, accessible regions, and large grafted groups disturb how the cellulose chains pack together. Lower crystallinity usually helps, because the material swells more and the binding groups are easier to reach.⁷³ However, if too much crystallinity is lost, the adsorbent can become mechanically weak.

SEM and BET are used to see how grafting changes the pores and surface area, since these affect how fast boron is taken up.⁷⁴ For example, a bacterial cellulose/zeolite imidazolate framework (BC/ZIF-8) composite had a BET surface area of 391.89 m²/g.⁸⁰ The surface charge, measured as the point of zero charge (pH_{pzc}) or the zeta potential, shows how much electrostatic attraction contributes to borate uptake.⁷⁵ For instance, a NMDG modified BC cellulose (MGMC) had a pH_{pzc} of 6.9.⁷⁶ After boron is adsorbed, the formation of borate esters can be confirmed in several ways: new B-O bands in the FTIR spectrum, a B1s signal in XPS, and when available, ¹¹B NMR, which can tell apart trigonal and tetrahedral boron.⁷⁶

ADSORPTION PERFORMANCE, MECHANISM AND KINETICS

Table 2 summarises the performances and operating parameters of the main cellulose-based materials reported for boron removal. In this section, the effect of pH is discussed first, and the materials are then compared by class, starting with unmodified cellulose, to cellulose derivatives, cellulose composites and cellulose-based membranes.

Effect of pH and boron speciation

The efficiency of boron removal depends strongly on solution pH, which governs boron speciation. At low concentrations typical of water treatment, boron is present almost entirely as either neutral boric acid (H₃BO₃) or the borate anion (B(OH)₄⁻), with a pK_a of about 9.2 at 25 °C.⁸³ Boric acid predominates under acidic and neutral conditions, while borate becomes the dominant species at higher pH. Because tetrahedral borate forms more stable esters with vicinal diols than trigonal boric acid does, most boron-selective adsorbents perform best in the near-neutral to mildly alkaline range (pH 6-10), where the proportion of borate increases and both species coexist. Accordingly, the optimal pH, for most cellulose-based adsorbents falls between 7 and 10, which conveniently overlaps with the natural pH of seawater.

Table 2
Performance metrics and operating parameters of key cellulose-based adsorbents and membranes
for boron removal

Adsorbent/ Membrane	Cellulose type	Opt. pH	Capacity (mg/g)	Temp. (°C)	Duration	Remarks	Refs.
A-NCC platelet shaped gels	CNC/CNF	7	120.9	30	120 min	Amino modified nanocellulose; Alkaline coagulation; 4 cycle reusability with 0.01M NaOH	77
CA@NMDG (cellulose acetate + NMDG)	CA	9	42.16	25	2h	Rapid initial adsorption; GMA epoxide ring opening functionalization	78
IL-CNC@DP (ionic liquid CNC, from date pits)	CNC	6	~25	25	60 min	Biowaste derived; Ionic liquid surface modification; High selectivity	79
MGMC (NMDG modified BC cellulose)	Bacterial cellulose	8	~1647 μmol/g	25	30 min	Fast adsorption; 6 regeneration cycles; Superior selectivity in brine	76
BC/ZIF-8 composite	Bacterial cellulose	7-9	BET: 391.89 m ² /g	25	60 min	ZIF-8 on BC scaffold; 6-cycle NaOH/EtOH regeneration; XRD/TGA confirmed stability	80
MCC (Microcrystalline cellulose)	MCC	11	1.3 – 3.0	25	120 min	Basic condition is required	63
B-MPCMIP (magnetic porous cellulose MIP)	MPC	7	High selectivity	25	60 min	Molecularly imprinted polymer; Magnetic separation	81
APCNC-TFN membrane (PA+amino-polyol CNC)	CNC	7	76.7% B rejection	25	continuous	Single pass, neutral pH, RO; Electrospray fabrication; No bulk pH adjustments	66
P(GMA-NMG) regenerated cellulose membrane	Regenerated cellulose	8-9	2-4 mg/g	25	continuous	LPR-UF system; Applicable to SWRO permeate post-treatment	64

Unmodified cellulose

Unmodified microcrystalline cellulose has a maximum capacity of only 1.3-3.0 mg/g, adsorbs boron effectively only under strongly basic conditions (pH ≥ 11), and requires about 10 h to reach equilibrium at room temperature.⁸⁴ These values illustrate the weak affinity of the trans-oriented hydroxyl groups of the cellulose backbone and provide the baseline against which the modified materials discussed below should be judged.

Cellulose derivatives

Amine-functionalised nanocellulose exhibited the highest adsorption capacities. Amino-modified nanocellulose (A-NCC) gels with platelet morphology, prepared by grafting primary amines onto the cellulose backbone followed by alkaline coagulation, showed optimum performance at pH 7, as established by Taguchi design and one-factor-at-a-time (OFAT) optimisation. Under the optimised conditions (30 °C, 80 mg adsorbent, initial boron concentration of 100 mg/L and 120 min contact time), 87.38% of the boron was removed, corresponding to a capacity of 120.9 mg/g.⁷⁷ Amino-polyol-functionalised cellulose nanocrystals (AP-CNC) offered the best compromise between capacity and

kinetics at pH 9 and remained effective across pH 7-9 at approximately 30 °C, although their maximum equilibrium capacity of 50 mg/g was reported at pH 2.

Among the NMDG derivatives, cellulose acetate functionalised with NMDG through GMA (CA@NMDG) achieved a maximum capacity of 42.16 mg/g at pH 9.0 and 25 °C with an adsorbent dosage of 2 g/L.⁷⁸ Uptake was rapid, reaching approximately 34 mg/g within 10 min, and equilibrium was attained within 2 h. A ribose-modified analogue (CA@Ribose), tested under the same conditions, reached only 17.9 mg/g, which highlights the superior boron affinity of the NMDG ligand.⁸⁵ The NMDG-modified bio-adsorbent (MGMC), tested at pH 8.0 with a dosage of 1 g/L, exhibited a capacity of 17.8 mg/g, exceeding that of many commercial adsorbents. It reached equilibrium within only 30 min at 25 °C, making it suitable for boron recovery from desalination waste streams.⁷⁶

Ionic-liquid-modified cellulose nanocrystals derived from date pits (IL-CNC@DP) performed best at pH 6, removing 97% of the boron.⁸⁶ A maximum capacity of 97 mg/g was obtained at an initial boron concentration of 100 mg/L, an adsorbent dosage of 1 g/L and a contact time of 24 h.⁸⁷ The capacity was highest at 25 °C, although varying the temperature between 25 and 45 °C had no significant effect, and the adsorption process was found to be exothermic and spontaneous.⁸⁸

Cellulose composites

In composite adsorbents, cellulose is combined with a second phase that contributes a specific function. The CNC-g-PAA/PEI-PVA hydrogel (CPPP), in which CNCs grafted with poly (acrylic acid) are combined with polyethyleneimine and poly (vinyl alcohol), achieved a capacity of 46.48 mg/g at pH 9.⁸⁹ This capacity was highest at 45 °C and equilibrium was reached after 3 h. The magnetic porous cellulose molecularly imprinted polymer (B-MPCMIP), in which magnetic porous cellulose serves as both the carrier and functional monomer, showed high affinity at pH 8.5 and reached equilibrium within 30 min in static tests using 2 mg of adsorbent per mL of buffer.⁸¹ Although its capacity was modest (4.4 mg/g), magnetic separation simplifies recovery of the adsorbent. In the BC/ZIF-8 composite, bacterial cellulose acts as a scaffold for the zeolite imidazolate framework, providing a high surface area and good stability during regeneration.⁸⁰

For comparison, a non-cellulosic benchmark, boron-modified Mg-Al layered double hydroxide (B Mg-Al-CLDH), was optimised by response surface methodology, which gave an optimal pH of 7, contact time of 200 min at room temperature and an optimal adsorbent dosage of 800 mg/L.⁹⁰ Such inorganic adsorbents lack the renewable origin and ease of functionalisation that cellulose offers.

Cellulose-based membranes

In liquid-phase polymer-based retention (LPR), also known as polymer-enhanced ultrafiltration (PEUF), a water-soluble NMDG-bearing polymer, P(GMA-NMDG), binds boron and the resulting complexes are then held back by a regenerated cellulose membrane. The process works best at pH 9.5 and room temperature, conditions under which boron exists mainly as borate. At a polymer to boron molar ratio of 40:1, it retained 2.0-4.0 mg of boron per gram of polymer under the same conditions.^{91,92}

Nanocellulose has also been incorporated into RO membranes. A polyamide membrane containing carbon nanotubes and cellulose nanofibers (CNT-CNF-PA) was tested at 25 °C. High boron rejection required a pH above 9 and was further improved by a higher operating pressure about 5.5 MPa, reaching roughly 85.4%.⁹³ A PVA membrane containing nanocrystalline cellulose (NCC)/gum arabic (GuA) conjugates rejected up to 92.4% of the boron in 8 h permeation tests, with the best results obtained at 0.06 wt% NCC and 0.04 wt% GuA. An amino-polyol CNC-modified thin-film nanocomposite membrane (APCNC-TFN), fabricated by electrospraying achieved 76.7% boron rejection in a single-pass operation at neutral pH, with no need to adjust the pH of the bulk solution.⁹⁴

Mechanisms and kinetics of boron uptake

Taken together, these studies show that functionalisation, especially with polyol or amine-polyol groups such as NMDG, raise the boron removal capacity of cellulose by one to two orders of magnitude, bringing it to levels that match or exceed those of commercial resins. The reported capacities, however, were measured under very different conditions and mostly in synthetic single-solute solutions, which makes direct comparison between materials difficult.

In the most selective materials, boron is removed mainly by chemisorption through complexation with vicinal diols assisted by amine groups. Both borate anions and neutral boric acid react with the vicinal diols of the adsorbent to form stable chelate complexes.⁹⁵

In NMDG derivatives, such as N-OPW, CA@NMDG, MGMC, CVN, and P(GMA-NMDG), the hydroxyl groups of the glucamine ligand form stable complexes with boric acid or borate.⁹⁶ In the amine-functionalised derivatives (A-NCC and AP-CNC) and the CPPP composite, protonated amine groups play an additional role. Under acidic to neutral conditions, the ammonium groups can bind boric acid or attract borate anions electrostatically to form ammonium-borate complexes, so the electrostatic contribution depends on both the boron speciation and the surface charge of the adsorbent.⁹⁷ Batch studies generally report pseudo-second-order kinetics and Langmuir-type monolayer isotherms, which is consistent with chemisorption on a finite number of equivalent sites. Uptake rates vary widely, with equilibrium reached in as little as 30 min (MGMC, B-MPCMIP) or as long as 10-24 h (MCC, CVN, IL-CNC@DP), reflecting differences in ligand accessibility and particle size. The thermodynamic behaviour differs as well, the adsorption on IL-CNC@DP was exothermic, whereas the capacities of CPPP and B-MPCMIP increased with temperature up to 45 and 40 °C, respectively.

In the membrane process, boron is removed by complexation, physical adsorption and size or diffusion based exclusion.⁹⁸ In LPR, water soluble polymers capture the boron species which are then separated by a regenerated cellulose membrane.⁹⁹ The soluble polymers P(GMA-NMDG) and P(GMHP) carry N-methyl-D-glucamine (NMDG) ligands, and the main mechanism is pH-dependent complexation. It is strongest at around pH 9.5, where borate predominates and interacts strongly with the hydroxyl groups of the NMDG ligand.^{100,101} The resulting high-molecular-weight boron polymer complexes are too large to pass through the filtration membrane and are therefore retained.¹⁰²

In RO membranes, boron rejections rely mainly on physical exclusion and charge repulsion, both of which depend on the size and charge of the boron species. The nanomaterials used to modify the membranes can reject further. In the CNT-CNF-PA membrane, the CNT and CNF structure suppresses hydrogen bonding between the polyamide matrix and boric acid, which limits the diffusion of boric acid. In the PVA/NCC-GuA membrane, the high rejection is attributed to a closely packed structure, formed by intermolecular hydrogen bonding among the many hydroxyl groups of the NCC, GuA and PVA chains, which physically hinders the passage of boron.¹⁰³⁻¹⁰⁵

REGENERATION AND REUSABILITY OF CELLULOSE-BASED COMPOSITES

Regeneration and reuse are essential if cellulose-based adsorbents are to be economically and environmentally viable in desalination post-treatment.¹⁰⁶ Because borate ester formation is reversible, the boron-adsorbent bond can be broken simply by changing the pH. Acidic elution or alkaline desorption (0.01-0.1 M NaOH) followed by re-conditioning is therefore the standard protocol for all classes of materials, and most systems retain more than 85% of their original capacity over four to ten consecutive cycles.

Among the cellulose derivatives, A-NCC was regenerated with 0.01 M NaOH and reused for at least four cycles.¹⁰⁷ MGMC eluted with dilute acid and then washed with alkali remained effective after five cycles, while N-OPW kept its removal capacity over three cycles, even in real geothermal water. Among the composites, the CPPP hydrogel was regenerated with HCl at pH 4 and neutralised with 0.01 M NaOH and reused for ten cycles.¹⁰⁸ The BC/ZIF-8 composite retained its BET surface area and its crystalline ZIF-8 structure after six cycles, as confirmed by XRD and TGA, which indicates that the bacterial cellulose scaffold protects the framework against repeated acid and alkali exposure.⁸⁰

In LPR systems, the water-soluble polymers are regenerated by lowering the pH to release the bound boron and tests on real samples confirmed that they can be reused efficiently.¹⁰⁹ For comparison, the non-cellulosic B Mg-A1-CLDH adsorbent was regenerated with 0.01 M NaOH for 30 min and reused for five cycles. Regeneration produces concentrated acidic or alkaline boron-containing eluates, and their treatment or valorisation has rarely been addressed.

CHALLENGES AND FUTURE PERSPECTIVES

Despite the advances discussed in this review, several research gaps must be closed before cellulose-based materials can be used in desalination plants. The main challenges and the research directions they suggest are outlined below.

Performance under realistic conditions and at neutral pH

Cellulose composite membranes have not yet brought boron below 0.5 mg/L in single pass RO at pH 7 with real seawater, and many adsorbents perform best only at pH 8-10. Most studies are batch experiments in synthetic single-solutions often at concentrations (up to 100 mg/L) far above those of seawater (4-6 mg/L) or SWRO permeate, and only a few have used real matrices. Long-term stability and resistance to salinity, competing ions, organic matter and temperature variations therefore remain uncertain. Future work should prioritise ligands that bind boric acid efficiently at pH 7-8 and report performance in real seawater or SWRO permeate.

Scale-up and integration into desalination processes

To our knowledge, none of the adsorbents in Table 2 has been tested at pilot scale in continuous fixed-bed columns with real SWRO permeate, so key design data, such as breakthrough curves, bed capacity, pressure drop and long-term stability are still missing. Equilibrium times range from 30 min to 24 h, and slow kinetics would mean large columns. The form of the material also matters, for example, nanocellulose powders and gels have a high surface area, but are hard to separate and cause high pressure drops, whereas beads, microspheres, aerogels, membranes and magnetic composites are better suited to continuous operation.

Cellulose-based adsorbents fit best as a post-treatment step for SWRO permeate or thermal distillate, where they could replace or supplement the second alkaline BWRO pass or synthetic boron-selective resins, provided they work at the near neutral pH of the permeate. Treating only part of the permeate and blending it with the rest would reduce the amount of adsorbent needed. Cellulose-modified membranes could instead be built directly into the membrane, but with current boron rejections of 76.7-92.4%, they still need alkaline conditions or extra stages to meet the strictest limits.

Sustainability and economic assessment

Life cycle and techno-economic assessments comparing cellulose-based systems with conventional membranes, two-pass RO or synthetic resins are largely missing. Such assessments are highly necessary before validating the application of such systems, as cellulose extraction and functionalisation consume chemicals and energy, and generate effluents. Biomass variability and the cost of grafting reagents, such as NMDG and GMA, also need to be addressed before industrial production.

Boron recovery and valorisation

Recovering boron from regeneration eluates remains largely unexplored. Producing boric acid from these concentrated streams could reduce waste disposal and improve process economics, particularly when brines or desalination waste streams are treated.

Computational and data-driven material design

Molecular simulation and machine learning have not yet been applied systematically to the design of cellulose functionalisation strategies and composites for boron removal. These tools could help identify ligands and spacer structures with higher selectivity for boric acid at neutral pH, predict the effect of competing ions and reduce the experimental effort needed to optimise grafting density and material form.

CONCLUSION

Boron removal remains a persistent challenge in seawater desalination. The problem is, at seawater pH, boron exists mainly as small, uncharged boric acid, which passes through standard polyamide RO membranes, so single-pass SWRO permeate often fails to meet the WHO drinking water guideline (2.4 mg/L) and irrigation limits (0.3-1.0 mg/L). Conventional solutions, namely two-RO under

alkaline conditions and boron selective resins, are effective, but carry significant chemical, energy and environmental costs.

Cellulose and nanocellulose, obtained from abundant agricultural residues, are promising platforms for boron-selective materials due to their hydroxyl rich surface, high surface area and versatile form. Unmodified cellulose adsorbs only 1.3-3.0 mg/g of boron, so surface functionalisation is the decisive step. Grafting NMDG, amine or amino-polyol groups raises the capacity to 17.8 mg/g for MGMC, 42.16 mg/g for CA@NMDG, 46.48 mg/g for A-NCC. Composites add functions such as magnetic separability and structural stability, and cellulose-modified membranes have reached boron rejections of up to 92.4%. Most adsorbents can be regenerated by simple pH cycling and reused for four to ten cycles.

The main remaining challenges are related to performance at neutral pH in real seawater, continuous and pilot scale validation, life cycle and techno-economic assessment, boron recovery from regeneration eluates, and computational material design. Addressing them will determine whether cellulose-based materials can move from promising laboratory adsorbents to practical components of sustainable desalination systems.

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