

Review of Inexpensive Adsorbents for Removing Boron from Aqueous Solutions

Nam-Il Kim^{1,*}, Kyong-Chol Kim²

¹Institute of Building Materials, State Academy of Sciences, Pyongyang, Democratic People's Republic of Korea

²Faculty of Applied Chemical Engineering, Kim Chaek University of Technology, Pyongyang, Democratic People's Republic of Korea

Email address:

kni19850315@163.com (Nam-Il Kim)

*Corresponding author

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Abstract: Boron is one of the essential elements for plants, animals, and humans, but its excess poses a great risk to life. Therefore, it is necessary to effectively remove boron from various boron-containing aqueous solutions to reduce damage to living things. There have been many studies on the adsorbent for removing boron from the boron-containing aqueous solution, but many of them are expensive or cannot be industrialized or commercialized, so they remain in the laboratory stage. Reducing the cost of adsorbent and realizing commercialization can be said to be the key links to successfully solving the problem of boron removal from an aqueous solution. The purpose of this review is to conduct a comprehensive analysis of inexpensive adsorbents used for boron removal from industrial wastewater and drinking water and to discuss future research directions. This article summarizes the development and utilization of inexpensive adsorbents, including inorganic materials, natural materials, and wastes. The limitations of performance, applicable conditions, sources, et al., of inexpensive adsorbents currently developed and utilized were analyzed, and future research directions were discussed. Most inexpensive adsorbents have a limited range of use, and compared to organic materials, inorganic materials have very low adsorption performance. The development of adsorbents using natural materials or waste is not active. Therefore, further research is needed to improve the performance of inorganic adsorbents, develop environmentally sustainable and efficient adsorbents, and recycle adsorbents.

Keywords: Boron Removal, Adsorbent, Inorganic Substance, Natural Material, Waste

1. Introduction

1.1. Distribution and Presence of Boron

In nature, boron is a trace element that is widely dispersed in the Earth's hydrosphere and lithosphere, primarily in compounds with other elements (such as boric acid or borates) [1-4]. Boron may be found in soil or rocks in the lithosphere, and its average concentration in the earth's crust is 10mg/kg, accounting for just 0.001% of the earth's elemental makeup [5, 6]. Boric acid, borax, borax hydrates, and sodium perborates are boron compounds that are economically important [7]. Boron has many minerals, mostly calcium and/or sodium borates, such as colemanite ($2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), ulexite ($\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$) and tincal ($\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$), etc. Its typical concentration in the hydrosphere is around 4.5 mg/L in salt water, and it ranges from 0.3 to 100 mg/L in

groundwater [5, 6, 8]. High levels of boron are found in seawater (4.7mg/L), domestic wastewater (0.5-2mg/L), and regional groundwater (e.g., Italy, Cyprus and Greece with boron content up to 8mg/L) [9].

In an aqueous solution, boron exists in the form of various borate salts such as $\text{B}_2\text{O}(\text{OH})_6^{2-}$, $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$, $\text{B}_5\text{O}_6(\text{OH})_4^-$ depending on the pH and boron concentration of the solution [10].

Boric acid is the major boron specie in acidic and neutral aqueous solutions. Boric acid is a solid that may be dissolved in water with a solubility of 55 g/L at 25°C. Because the pK_a in aqueous solutions is less than 9.24, boron acid is a weak Lewis acid [Eq (1) [4]], which receives a hydroxide ion and releases a proton. Boric acid's pK_a value may be calculated at low concentrations, notably below 22 mg/L [11]. Boric acid converts into a monoborate anion in alkali aqueous solutions. The monoborate anion is the predominant boron species when

the pK_a exceeds 9.24 [12].

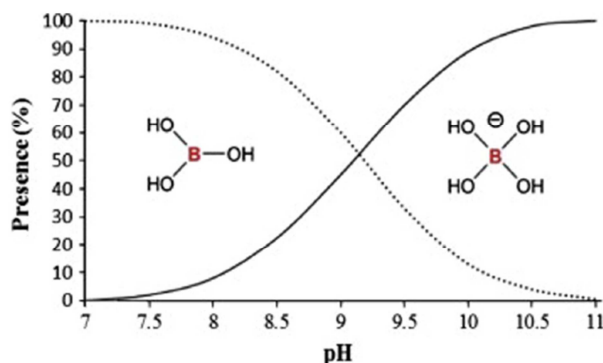


Figure 1. Distribution diagram of boric acid and borate ions in solution at various pH [13].

As shown in Figure 1, at low pH, boric acid dominates, whereas borate ion dominates at high pH. In addition, $B(OH)_3$ and $B(OH)_4^-$ low concentration (<216mg/L). At high concentrations (>290mg/L), there are many boron species in boron solutions, such as $B_2O(OH)_6^{2-}$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$, and $B_5O_6(OH)_4^-$ [8, 10, 14]. Most borate anions may be detected when the pH is raised above the pK_a value [15].

1.2. Field and Situation of Boron Utilization

Boron is a chemical and biological element having several applications in modern industries. Boron and boron compounds are widely used in over 100 industries, including glass, electronics, ceramics, enamels, porcelains, cosmetics, semiconductors, leathers, pharmaceuticals, insecticides, catalysts, fuels, cleaning products, corrosion inhibitors in anti-freeze formulations for motor vehicles and other cooling systems, buffers in pharmaceutical and dyestuff production, nuclear reactor moderators, and so on. The glass sector is the largest user, accounting for more than half of the total boron compound output [16-20]. Boron compounds are widely utilized in photography chemicals and the production of fireproof textiles. Boric acid, which has moderate bactericidal and fungicidal effects, is used as a disinfectant and food preservative, and a substantial quantity of boric acid is utilized in the polarizer production process as a complex combination with iodide [18]. Borax is commonly used in metal welding and brazing [17]. Boron and its compounds are key fundamental raw materials for a variety of industries due to their outstanding properties such as flame retardance, heat and wear resistance, high strength, and rigidity [19, 20]. Furthermore, they are exploited as an alternative energy source, and new boron use sectors are being discovered [7].

1.3. Importance of Boron

1.3.1. Advantages

Boron, a crucial element for plants, animals, and people, has a twofold influence on the earth's biological processes

[21].

Boron has a noticeable influence on plants. Boron absorption is required during plant germination, development, and fruit setting [22], and it is involved in carbohydrate metabolism, sugar translocation, hormone action, proper apical meristem growth and function, nucleic acid synthesis, and biological membrane structure and function [15, 23]. Boron shortage can harm plants by slowing root and leaf development, cracking bark, slowing enzyme reactions, inhibiting leaf photosynthesis, and can even cause plant death [4, 15, 24]. Boron affects numerous other plant activities, including reproductive development and stimulation, seed quality, and biosynthesis [25, 26].

Boron's effects on animals have not been studied as thoroughly as they have on plants. Boron affects the immunological function of organisms in both animals and humans [27], as well as bone metabolism and central nervous system function [28]. Boron deficiency can induce abnormalities in vertebrate embryos [29] as well as inadequate absorption efficiency for nutrients including calcium, magnesium, and phosphorus [4, 8]. Boron is also required by animals to maintain the appropriate function of the cell membrane and to aid calcium and magnesium metabolism in animal bodies [30, 31].

Boron is essential for the metabolism of calcium for human bone structure, as well as the enhancement of brain function, psychomotor reaction, and the response to estrogen consumption in postmenopausal women. It is also useful in the treatment of several types of arthritis [15, 32]. Furthermore, boron contributes to human body metabolisms such as calcium, magnesium, amino acids, glucose, and certain hormones. As a result, inadequate boron consumption causes incorrect bone formation, low hormone levels, increased calcium concentration in urine, and variations in micro mineral status, among other things [25, 26].

1.3.2. Disadvantage

Although boron absorption is required for all forms of life on Earth, including people, animals, and plants, as indicated in Table 1, the difference between boron insufficiency and boron toxicity is thin and varies widely by species [33]. As a result, it becomes harmful for organisms when the boron concentration is somewhat greater, and toxicity effects induced by excess boron are more widespread in the environment than by boron shortage.

Plants require just a very low boron level in their irrigation water for metabolic activity. Boron poisoning will impair plant growth by causing edge and tip necrosis and yellowing patches in the leaves, reducing root cell division and dwarfing, followed by lower photosynthesis and less yield, even plant mortality, and so on [15, 17, 34-37].

Although the mechanism of toxicity induced by excess boron is unknown in people and animals, long-term excessive boron consumption can impair the human central nervous system and reproductive system [9, 36, 38-41]. Furthermore, it alters blood composition, stunts child growth, increases the risk of birth pathology in pregnant women, and affects human

fetuses throughout pregnancy [26, 42, 43].

Table 1. Tolerant of various commercial crops to boron content in irrigation water [26].

Maximum allowable boron concentration (mg-B/L)	Commercial crops		
< 0.5	Blackberry	Lemon	
	Apricot	Avocado	Cherry
	Garlic	Grape	Grapefruit
	Onion	Orange	Peach
0.5-1.0	Persimmon	Plum	Sweet potato
	Walnut	Wheat	
	Carrot	Cucumber	Pea
	Pepper	Potato	Radish
1.0-2.0	Artichoke	Cabbage	Celery
	Lettuce	Maize	Mustard
	Oats	Tobacco	Turnip
	Alfalfa	Beet red	Parsley
2.0 - 4.0	Sorghum	Tomato	
	Asparagus	Cotton	

1.4. Criteria for Boron

Considering the effects of boron on living organisms and the environment, the WHO and many countries set guidelines for limiting values of boron in irrigation water, drinking water, and wastewater (Table 2).

Boron is typically absorbed by plants through irrigation water, and the difference between boron shortage and boron toxicity is quite narrow. Boron concentrations in irrigation water that are safe for sensitive plants are 0.3mg/L, 1-2mg/L for semi-tolerant plants, and 2-4mg/L for tolerant plants [17]. Boron levels in irrigation water that surpass 1mg/L can reduce the output of sensitive crops (e.g., avocado and citrus fruits) [9]. Lemon and blackberry plants cannot tolerate boron concentrations above 0.5mg/L (extremely sensitive plants); orange, peach, cherry, plum, onion, and grape plants can only tolerate boron concentrations up to 0.75mg/L (very sensitive plants); but sorghum, cotton, celery, and asparagus can tolerate boron concentrations up to 10mg/L (very tolerant plants) [5].

A proper boron level would be good for organisms, while too much boron might create major difficulties. The WHO increased the boron recommendation value in drinking water to 2.4 mg/L in 2011 [39, 41, 44]. However, just a few nations implement the WHO suggestion, with Saudi Arabia being the sole exception [5]. Because the value of 2.4mg/L surpasses the acceptable concentration of many crops, particularly in low annual rainfall countries such as South and South-West Asia and Africa, where desalination facilities supply a substantial amount of irrigation water [5]. Boron restrictions in the European Union, the United Kingdom, and Japan are 1.0mg/L. In the United States, there are no federal boron limits, and boron standards vary from state to state, ranging from 0.6 to 1.0mg/L [8]. Canada, Brazil, and Australia have established boron content recommendations as high as 5mg/L, 5mg/L, and 4mg/L, respectively, much beyond the WHO limit [5, 45].

Some countries have also established boron requirements in effluent from human activities. High boron concentrations, for example, have been identified in the effluent of various businesses, including semiconductor, ceramic, borosilicate

glass, and detergent producers. The Environmental Protection Agency (EPA) of Taiwan has set a boron discharge limit of 1mg/L [31, 46, 47]. Boron effluent requirements in Japan are 10mg/L in non-coastal areas and 230mg/L in coastal areas [48], while the recommended boron concentration in industrial wastewater effluent is 10mg/L [21, 41]. In Indonesia, the boron effluent limit is similar to 1mg/L [47].

Table 2. Regulated boron content allowed in drinking water by region (mg-B/L).

Region	Drinking water	Effluence ^a
WHO	2.4 [49]	
	1 in California	
	0.9 in Wisconsin	
USA ^b [50]	0.63 in Florida, Maine and New Hampshire	–
	0.6 in Minnesota	
	1 [50]	–
European Union	5 [50]	–
Canada	1.4 [50]	–
New Zealand	4 [50]	–
Australia	1.0 [50]	10 [51]
Japan	2.4 [52]	5.0 [53]
Singapore	0.3 [11]	1.5 [51]
Israel	–	5.0 [51]
Brazil	0.5 [54]	4.0 [51]
Malaysia	0.5 [55]	2.0 [51]
India		

^a Excluding the water protection area, effluent to surface water.

^b Boron in drinking water is not regulated by the federal government.

1.5. Anthropogenic Emissions of Boron

Boron pollutants in water have two sources: one natural and one caused by human activity [3]. In 2016, humans contributed more than 90% of crustal input flux for industrial purposes, totaling 2.3Tg-B. Boron mining (0.7-1.5Tg-B/year), exploration-produced water and gas and oil production (0.75Tg-B/year), and coal mining (0.4Tg-B/year) are the primary anthropogenic sources. Although human civilizations retain or waste up to 0.7Tg-B each year, it is estimated that 0.8Tg-B is discharged into rivers yearly, accounting for approximately 80% of river flows to the ocean. Municipal wastes high in detergents and cleaning goods are the most

common sources of boron in surface waterways, followed by industrial wastes from a variety of various activities and many chemical compounds used in agriculture. Boron pollution in the surface water is a major concern since it endangers the aquatic ecology and raises the boron content in the drinking water source. Table 3 depicts the normal boron range in wastewater, which is substantially higher than the discharge limitations reported in Table 2. The produced water from the extraction of gas and oil by hydraulic fracturing includes hundreds of mg-B/L due to the usage of borate-based cross-linkers (Table 4). Coal-fired power facilities are possible sources of anthropogenic boron emissions. Because boron is an impurity in coal, and because the majority of

coal-fired power plants employ wet lime scrubbing technology to achieve flue gas desulfurization (FGD), boron is discharged into the FGD wastewater at concentrations of up to 400mg-B/L. (Table 5). As demonstrated in Table 6, various investigations found boron and arsenic in geothermal and hot spring water [33]. Boron-containing wastewater is also produced by several sectors, including mining and refining, metal processing, TFT-LCD, and semiconductor. Although the production rate of boron-containing wastewater is lower than that of generated water and FGD wastewater, the complicated composition and exceptionally high boron concentration make treatment challenging (Table 7) [26].

Table 3. Boron content range of the main boron rich streams [26].

Industry	Boron (mg-B/L)	Other constituents
Oil/gas excavation	100–400	TSS and TDS
Coal-fired power plants	30–400	F ⁻ , NO ₃ ⁻ , COD and TSS
Geothermal water	20–600	Arsenic and silicate
Mining	2000–7000	Arsenic
TFT-LCD	600–1000	Iodine
Metal-processing	10–100	Metals (Zn and Sr)
Semiconductor	600–5000	Metals (Co and Ni)

Table 4. Produced water composition reported in the literatures.

Location	U.S./Canada					Malaysia	U.S.
Boron (mg/L)	400	429	350	404	311	15	123
pH	5.9	6.2	6.5	5.4	5.1	7.8	7.8
Total dissolved solid (mg/L)	3.2×10 ⁵	3.2×10 ⁵	2.3×10 ⁵	5.0×10 ⁵	2.5×10 ⁵	1.6×10 ⁴	2.9×10 ⁴
Total hardness (mg/L as CaCO ₃)	5.8×10 ⁴	6.0×10 ⁴	4.4×10 ⁴	4.4×10 ⁴	4.2×10 ⁴	-	2920
Reference	[56]	[56]	[56]	[56]	[56]	[57]	[58]

Table 5. Composition of flue gas desulfurization wastewater from coal-fired power plants.

Location	Hong Kong	U.S.		Poland	
pH	7.3	8.6	-	6.7	7.3
Boron (mg/L)	404	7.5	390	340	26.5
Fluoride (mg/L)	50	32	-	-	1.4
Sulfate (mg/L)	566	5064	-	1722	-
Chloride (mg/L)	1097	1233	-	12242	2160
Manganese (mg/L)	16	7	-	-	4.6
Nickel (mg/L)	1.7	15 ppb	-	1.2	-
Zinc (mg/L)	-	50 ppb	-	15.9	8.3
Nitrate (mg-N/L)	226	75	48	232	-
COD (mg/L)	226	-	240	395	128
Conductivity (mS/cm)	-	8.1	-	33.4	51
Reference	Received sample	[59]	[60]	[61]	[62]

Table 6. Composition of geothermal wastewater reported in the literature.

Location	Japan		Mexico			
Boron (mg/L)	24	450	500	158	279	580
Sodium (mg/L)	630	2830	1.5×10 ⁵	4300	4370	195
Calcium (mg/L)	55	76	1×10 ⁴	275	54	1.5
Arsenic (mg/L)	0.45	-	30	3.4	14.4	5.8
Chloride (mg/L)	353	3360	3×10 ⁵	7900	2700	73
Carbonate (mg/L as HCO ₃ ⁻)	904	-	-	30	12	110
Sulfate (mg/L)	242	57	170	18	43	78
Silicon (mg/L as SiO ₂)	107	-	4×10 ⁴	540	777	521
Reference	[63]	[64]	[33]	[33]	[33]	[33]

Table 7. Composition of boron-containing wastewater produced in various industries.

Industry	Location	pH	[B]	Remark	Reference
Mining and refinery	Turkey	7.2	2000	Arsenic=18.8mg/L	[65]
	Turkey	9.5	4000	-	[66]
	Turkey	8.7	7000	-	[67]
TFT-LCD	Taiwan	5.1	1050	Iodine=4100mg/L	[68]
	Taiwan	6.3	600	Iodine=6200mg/L	[69]
Metal processing	China	5.1	9.3	Zinc=9.6mg/L COD=125mg/L	[70]
	Taiwan	6.9	100	Strontium=417 ppm	
	Taiwan	12.4	570	NPDOC ^a =310mg/L	
Semiconductor	Taiwan	11.5	2300	Carbonate=1.0×10 ⁴ mg/L as CO ₃ ²⁻	Received sample
	Taiwan	3.2	4800	Cobalt=2678mg/L	
	Taiwan	5.9	3600	Nickel=5.5×10 ⁴ mg/L	

^a NPDOC=non-purgeable dissolved organic carbon

When wastewater with high quantities of boron compounds enters the drinking water source, boron accumulates in vegetable tissues, posing a possible health risk to individuals who consume boron-containing food and water, and can hurt plant development. Therefore, it is necessary to effectively remove boron from various boron-containing wastewaters to reduce damage to living things.

Because although Earth is composed mainly of water, only 1% of this is consumable freshwater, and the increasing demand for freshwater is a pressing concern [38]. So, boron removal is an important issue in desalination treatment to solve the global drinking water shortage problem.

This paper outlines the inexpensive adsorbents for removing boron from an aqueous solution developed and used so far in consideration of the economic aspect and discusses the future research direction.

2. Techniques for Boron Removal

Much research has been done over the last few decades to develop effective boron removal procedures, in light of the rising concentration of boron in surface waters and the necessity to treat saltwater containing substantial levels of boron. The high boron concentration in natural and effluent waters emphasizes the necessity of research to design and implement effective techniques for removing boron from aqueous media. Unfortunately, there is no simple or cost-effective solution to complete this work. The most challenging aspect of selecting this approach is that boron exists in water as a variety of compounds and its concentration changes from location to location [71]. Water purification procedures that are often used, such as precipitation on clay, coagulation, or adsorption on boron compounds, are ineffectual. Water treatment using biological or chemical chemicals is ineffective because they remove just a tiny quantity of boron or none at all [71, 72].

To summarize the effective techniques applied to boron removal in the past, there is adsorption [71, 73, 74], reverse osmosis (RO) [75-78], and ion exchange [79-85], electrocoagulation [58, 86-90], Donnan dialysis [91-93], chemical coagulation [3, 94], hybrid process [95, 96], polymer enhanced ultrafiltration (PEUF) [97-101],

adsorption membrane filtration (AMF) [72, 96, 102-111], and extraction by ionic liquids [112] etc. Adsorption is a particularly efficient way of removing boron from extremely low-concentration aqueous solutions in these approaches.

So far, the adsorbents used in the boron removal process include activated carbon, fly ash, clay, natural minerals, layered double hydroxides, biological materials, oxides, mesoporous silica, nanoparticles, composite membranes, and selective resins. In consideration of the boron removal capacity or regeneration, most of the boron removal uses boron selective resin or ion exchange membrane, and other inexpensive materials such as clay or biomass materials are not widely used. As mentioned above, boron removal is very important, but if the cost is high, it will not meet the economic requirements, and these technologies or materials will not be popular. It can not only achieve the goal of boron removal but also obtain economic benefits to recycle the waste or actively develop and utilize the adsorbent needed for boron removal by using inexpensive raw materials. There is much research on boron removal technologies or adsorbents using high-cost materials such as ion exchange membranes or boron selective resins, and many review papers have commented on them. However, there are few studies on inexpensive adsorbents and few papers on their comprehensive investigation.

In this work, with the cost of adsorbent as the basic focus, the inexpensive adsorbent developed so far for boron removal was comprehensively investigated, and the future research direction was discussed.

3. Adsorption Materials for Boron Removal

3.1. Inorganic Substances

3.1.1. Activated Carbon

Activated carbon (AC) has a high adsorption capacity due to its large specific surface area and is the most extensively utilized adsorbent in industrial and environmental applications. However, there have been few investigations on the use of activated carbon to remove boron. The

fundamental explanation for this is that activated carbon contains fewer boron surfaces and active groups than nonactivated carbon, resulting in reduced adsorption selectivity [4]. The removal capability and circumstances that regulate boron retention were examined using AC produced from olive bagasse by physical activation. The maximal boron removal capacity was 3.5mg/g at an initial pH of 5.5, and the experiment demonstrated that the adsorption kinetics suited both the pseudo-first-order model and the intraparticle diffusion model well [113]. The salicylic acid-impregnated AC was created to remove boron from aqueous solutions. In 10 minutes, the adsorption experiment reached equilibrium, and the experimental results closely matched the pseudo-second-order kinetic model. The experimental finding was also compatible with the Langmuir isotherm [114]. In the instance of aqueous boron adsorption employing multiple impregnated ACs, the best sorbent for the static system was AC impregnated with tartaric acid, whereas the best sorbent for the dynamic system was AC impregnated with mannitol [115]. The greatest boron removal was found in the investigation for batch and fixed-bed adsorption characteristics of boron on curcumin-impregnated activated carbon (Cur-AC) at pH 5.5 and 120 min of contact time. The Langmuir and Freundlich isotherm models were used, and the experimental data was shown to agree with both [116]. In addition, adding powdered activated carbon (PAC) as a pretreatment to a saltwater reverse osmosis (SWRO) process might improve the performance of the adsorption-MF system at high pH. Various commercial activated carbons (CAC) treated with mannitol or xylitol are effective boron adsorbents in contaminated water [117].

Physical or chemical treatment of activated carbon with a large surface area can not only improve the boron removal capacity but also be economical. However, the technology of recycling activated carbon adsorbent has not been developed. If boron removal activated carbon adsorbent is recycled, greater benefits will be obtained.

3.1.2. Oxides and Hydroxides of Metal

Numerous authors employed oxides and hydroxides with divalent and trivalent metal ions in boron adsorption because they are typical sorbents in industrial and environmental applications and have good adsorption capabilities on many materials [4].

Alumina is the most researched oxide adsorbent in the removal of boron. When activated alumina was used as the adsorbent, Bouguerra et al. [118] discovered that the maximum boron adsorption efficiency reached 65% for the 5g adsorbent dosage in the 50mg/L boron solution, whereas the maximum boron adsorption efficiency was 40% for the 0.8g adsorbent dosage in the 5mg/L boron solution. And discovered that the rate of boron adsorption increased with increasing pH. Seki et al. [119] came to the opposite conclusion. In addition, to remove boron, cerium oxide [120] and iron oxide [121] were utilized as sorbents.

In aqueous solutions, hydroxides can form complexes with $B(OH)_4^-$, making them boron-sensitive sorbents [4]. Tsai and

Lo [68] used two modified calcium hydroxide particles, with boron recovery efficiencies of 77.2% and 76.3% at 95°C. Furthermore, Lin et al. [122] found that using $Ba(OH)_2$ as sorbents lowered boron concentration from 1000ppm to 3ppm. Calcium borate minerals were collected by Itakura et al. [21] utilizing the hydrothermal mineralization technique by adding $Ca(OH)_2$ and/or H_3PO_4 to wastewater, resulting in the development of an ecologically viable boron removal technology. Yilmaz et al. employed $Ca(OH)_2$ as a precipitant to remove boron. At pH 1.0 and an initial boron content of 2500mg/L, the greatest boron removal rate was observed. Garca-Soto et al. [123] investigated the effects of magnesium/boron molar ratio, alkalizing reagent capacity, contact time, reaction temperature, solution pH, and the presence of other ions on boron adsorption by magnesium hydroxide. Abbas et al. [124] examined the boron removal capacity of magnesium, aluminum, and iron oxides, as well as the influence of operating settings on each material's boron removal efficiency. Maximum boron removal was reached at pH 9.5 for magnesium oxide and 8 for aluminum and iron oxide, according to the experimental data. Under the right circumstances, the proportion of boron adsorbed onto magnesium, aluminum, and iron oxide can approach 90, 42.5, and 41.5%, respectively.

As above mentioned, the cost of boron removal can be reduced by using divalent and trivalent metal hydroxides commonly seen in nature as adsorbents. However, when metal hydroxide is used as an adsorbent, it has an obvious removal effect on the aqueous solution with a higher boron concentration, but not on the aqueous solution with a lower boron concentration. In addition, the sediment after boron removal will become a secondary pollutant, which needs to be reprocessed.

3.2. Natural Materials

Numerous investigations on boron elimination using natural materials have also been conducted. Natural material adsorbents are classified into two types based on their material qualities. The first is natural minerals, while the second is plant stuff. Natural material adsorbents have been shown to be the prerequisites for inexpensive boron removal procedures in water treatment due to their vast range of sources and inexpensive prices [4].

Jalali et al. [125] employed bentonite, kaolinite, zeolite, waste calcite, and wheat, rice, and green shell of walnut wastes chemically treated with $FeCl_3$ as adsorbent for boron removal from aqueous solution. According to the experimental data, organic matter outperforms minerals in terms of boron adsorption. Masindi et al. [126] created a boron-removing composite from powdered bentonite and magnesite. Under ideal circumstances, the boron content fell from 5 mg/L to less than 0.01mg/L. Kıpçak and Özdemir [127] treated boron aqueous solutions with calcined magnesite at 600 °C. The maximal adsorption capacity at 45°C was determined to be 65.79mg/g. Karahan et al. [128] used clays and modified clays including bentonite and sepiolite to investigate boron adsorption performance in

aqueous solutions with high ionic strength and pH values in the 8-10 range. Öztürk and Kavak [129] employed inert waste sepiolite and HCl-activated waste sepiolite as boron removal adsorbents. It was established that the two most critical elements influencing the adsorption process are temperature and pH value and that raising pH is beneficial but the decreasing temperature is detrimental. The activated waste sepiolite was more efficient for boron removal since the specific surface area of sepiolite increased with acid activation. Another research found that when calcined alum is used to remove boron, the boron adsorption rate is around 49% under ideal circumstances, with a removal capacity of 3.39mg/g [130] and discovered that boron adsorption was significantly dependent on particle size when micron-grade vermiculite was utilized as the adsorbent [131]. Demey et al. [38, 132] employed chitosan and nickel(II) hydroxide [Ni(II)] and iron(III) hydroxide [Fe(III)], which are natural biopolymers with amino and hydroxyl groups. A boron adsorbent was created. Calcium alginate gel beads have also been demonstrated to be effective boron adsorbents [133, 134]. Tsai et al. [31] investigated the effects of the pretreatment method (heat or pyrolysis), particle size, initial boron concentration, reaction time, and shell capacity on boron recovery using three types of pre-treated (heated or pyrolyzed) clam shells (oysters, clams, freshwater clams) as a mineralizer to remove and recover boron from concentrated wastewater. Heat-treated oyster shells outperformed heated hard clam shells and freshwater clam shells. Some studies have investigated the use of plant materials for boron removal, such as date palm seed ash [135], PVA-functionalized pomegranate seed powder [136], and rice husk [137]. These substances are easily obtained in nature, and also have a certain boron removal capacity. However, if it is to be used as an adsorbent for boron removal, it must be treated by industrial methods, and its adsorption performance is not very high.

3.3. Wastes

Öztürk et al. [17] examined boron removal from aqueous solutions employing fly ash with particle sizes ranging from 250 to 400 μ m as the adsorbent. The batch sorbent dosage was determined to be 20.9mg/g, while the column study dose was calculated to be 46.2mg/g. Polowczyk et al. [16] evaluated the boron adsorption capability of FA particles ranging in size from 1.0 to 1.6 mm. The highest adsorption capacity was 6.9mg/g (0.0025 sorbents to solute ratio), while the highest removal rate was 90%. (0.75 sorbents to solute ratio). A new zeolite-based on FA was synthesized by Klucza et al. [138]. The clearance rate and adsorption capacity of boron were 2.3 mg/g and 93%, respectively. To remove boron from the solution, Yüksel et al. [139] utilized FA, zeolite, and desalted lignite, in that order. To remove boron from seawater, Polat et al. [9] carried out column and batch tests using coal and FA. According to the findings, coal and FA were successful in removing 95% of the boron. Ash from palm oil mill boilers (POMB) also falls under the category of industrial waste. In research employing technology to remove boron

from wastewater, the boron removal efficiency was found to be 65.69% [140], and the boron concentration was reduced from 15mg/L to 3mg/L [141]. For the elimination of boron, certain additional wastes are employed. Both materials may be employed as alternative adsorbents for boron removal, as demonstrated by Irwan et al. [142] who used aluminum-based water treatment residues (Al-WTRs) as adsorbents, and Iizuka et al. [143] who examined the boron absorption characteristics of broken waste concrete particles. Additionally, Fujita et al. [144] discovered that although activated sludge's adsorption data could be explained by the Freundlich and Langmuir isotherms, their capacity to remove boron was constrained.

The utilization of industrial wastes can save the cost of boron removal, obtain economic benefits, and have advantages in environmental protection. However, to use these wastes as adsorbents, a certain pretreatment process must be carried out, and when used alone, the adsorption performance is not high.

4. Discussion

In the past few decades, many researchers are interested in the adsorbent for removing boron from aqueous solutions and have carried out a lot of research in this field. In this paper, the inexpensive adsorbents used to remove boron from aqueous solution are divided into inorganic materials, natural materials, and waste materials.

Inexpensive adsorbents are easy to obtain in nature, low in price, and have the advantages of economy and environmental protection. However, like all things, these economical and environment-friendly materials also have a series of shortcomings.

First of all, the application conditions of most adsorbents are very limited. For example, it is greatly affected by the temperature, pH value, and initial boron concentration of the aqueous solution.

Secondly, compared with organic materials, the adsorption performance of inorganic materials is very low. For example, the specific surface area of activated carbon is large, but the contact time is very long in the process of boron removal. In addition, when using metal oxides or hydroxides, the adsorption performance of the solution with low boron concentration cannot play well. In this case, the sediment also has defects that may cause secondary pollution.

Thirdly, there are only a few kinds of natural materials or waste materials used as adsorbents. For example, the research on the active use of agricultural and industrial by-products such as grain straw or waste concrete is insufficient.

Fourthly, the research on inexpensive adsorbents is mostly limited to a single adsorbent, and the developed mixed adsorbent also has the disadvantage of high manufacturing costs. Moreover, research on the regeneration and recovery of inexpensive adsorbent for boron removal cannot be carried out at all.

5. Conclusions

This article summarizes the development and utilization of inexpensive adsorbents, including inorganic materials, natural materials, and waste. Due to economic and environmental advantages, inexpensive adsorbents have become a major concern, but without dissolving the drawbacks mentioned above, broad application prospects cannot be expected. Thus, the following issues have to be resolved in future research on inexpensive sorbents for boron removal:

First of all, in order to improve the boron selectivity, adsorption stability, and other adsorption properties of inorganic adsorbent, it should be studied. An inorganic adsorbent that is not affected by the initial boron concentration, working temperature, and pH value of the aqueous solution and can completely remove boron in a short time must be developed. It will be can actively use inexpensive materials such as activated carbon with a large specific surface area, iron oxide, calcium hydroxide, and so on.

Secondly, industrial and agricultural wastes should be actively used to develop environmentally friendly and sustainable adsorbents. As mentioned above, we can actively seek to utilize waste materials such as grain straw or waste concrete or other natural materials such as shells and orange peel. The problem here is to minimize the cost of processing these materials. If the cost of this pre-treatment project is high, its significance will be less.

Finally, the problem of adsorbent recycling that has not been researched so far is urgently put forward. Generally speaking, these inexpensive adsorption materials after boron removal, have been treated as waste. This may cause secondary pollution. If the boron in the sediment is recycled and the adsorbent is reused, it will be more economical and environmentally friendly. As a research trend, nano iron oxide particles are being used to remove boron.

In practical applications, the complexity and variability of environmental systems will continue to create problems to be solved in the future.

Highlights

- 1) An updated review of the inexpensive adsorbents for boron removal from aqueous solutions containing boron.
- 2) It is necessary to improve the boron selectivity, adsorption stability, and adsorption capacity of inorganic adsorption.
- 3) The industrial and agricultural wastes should be actively used to develop environmentally friendly and sustainable adsorbents.
- 4) The research on reducing the cost of hybrid adsorbents will also become a research focus, and the problem of recycling these inexpensive adsorbents will need to be solved in future research.

Conflict of Interest Statement

All the authors do not have any possible conflicts of interest.

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