University of California

Los Angeles

USE OF BORON IN DETERGENTS AND ITS IMPACT ON RECLAMATION

A thesis submitted in partial satisfaction of the requirements for the degree Master of Science in Civil Engineering

by

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1. Abstract

Recently, many parts of the world are experiencing severe water drought. Drought is affecting societies economically and environmentally. Issue of drought becomes more serious considering everyday increasing demand for fresh water. Therefore, conservation practices are essential to balance water supply and demand. Greywater, if treated well, can be a reliable source for some activities such as irrigation or car washing. The application of insufficiently treated water for irrigation can cause harms to plants and animals that become in contact with it. Pollutants such as boron, oil, salt and surfactants are commonly found in greywater. High concentrations of boron can induce toxicity in plants, so for the purpose of safe application of greywater, any proposed greywater treatment needs to consider boron removal from its source. This thesis reviews boron chemistry and its effect on plants. Particular focus is given to the review of current available boron removal technologies.

2. Introduction

Development of new reliable local resources is crucial to maintain increasing demand of freshwater. For instance, different available technologies for wastewater treatment enable us to reuse wastewater through reclamation and recycling. Reclaimed wastewater is suitable for a beneficial or controlled use that would not otherwise occur[1]. Treating greywater for irrigation application is one method to conserve water and reduce potable water consumption for landscape purposes. Broad definition of greywater consists of all non-toilet household wastewaters. It includes wastewater from showers, baths, hand basins, washing machines, laundry, dishwashers and kitchen sinks. Separation of greywater from toilet effluent permits more effective, affordable and uncomplicated on-site treatment due to lack of organic matter and nitrogen. However, a high concentration of surfactants, oils and boron have been observed in greywater as a result of extensive use of detergents[2]. Eriksson et al conducted an extensive review on the composition of greywater and they demonstrated that concentration of boron in greywater depends on its source and installation. However, boron concentration above 0.5 mg/l is not reported from any greywater sources[3]. Considering the importance of greywater reuse for arid areas such as Southern California, the aim of this study is to review environmental fate and effect of boron in greywater and also comparing boron removal performance using conventional and advanced technologies.

Boron is the first element of Group III, with atomic number of 5 and it is fairly abundant element in the Earth. It shares some similarities with aluminum (which is next element in Group III) due to its valence and properties that are related to that; however most of boron properties are analogous to those of Silicon and in some cases Germanium[4]. Boron can form compounds with oxygen, fluorine, bromides and chlorine as well as metals. The EPA[1] provides an extensive list of chemical and physical properties of boron compounds which are categorized in Table 1[5]. Among various boron compounds, boric acid, H_3BO_3, and borax, $Na_2B_4O_7.10H_2O$, are the most environmentally concerned compounds since other types of boron compounds are introduced to the environment in such small amounts that their environmental significance is minor. It should be noted that boric acid and borax are also products of the breakdown of other compounds in the natural environment[6].

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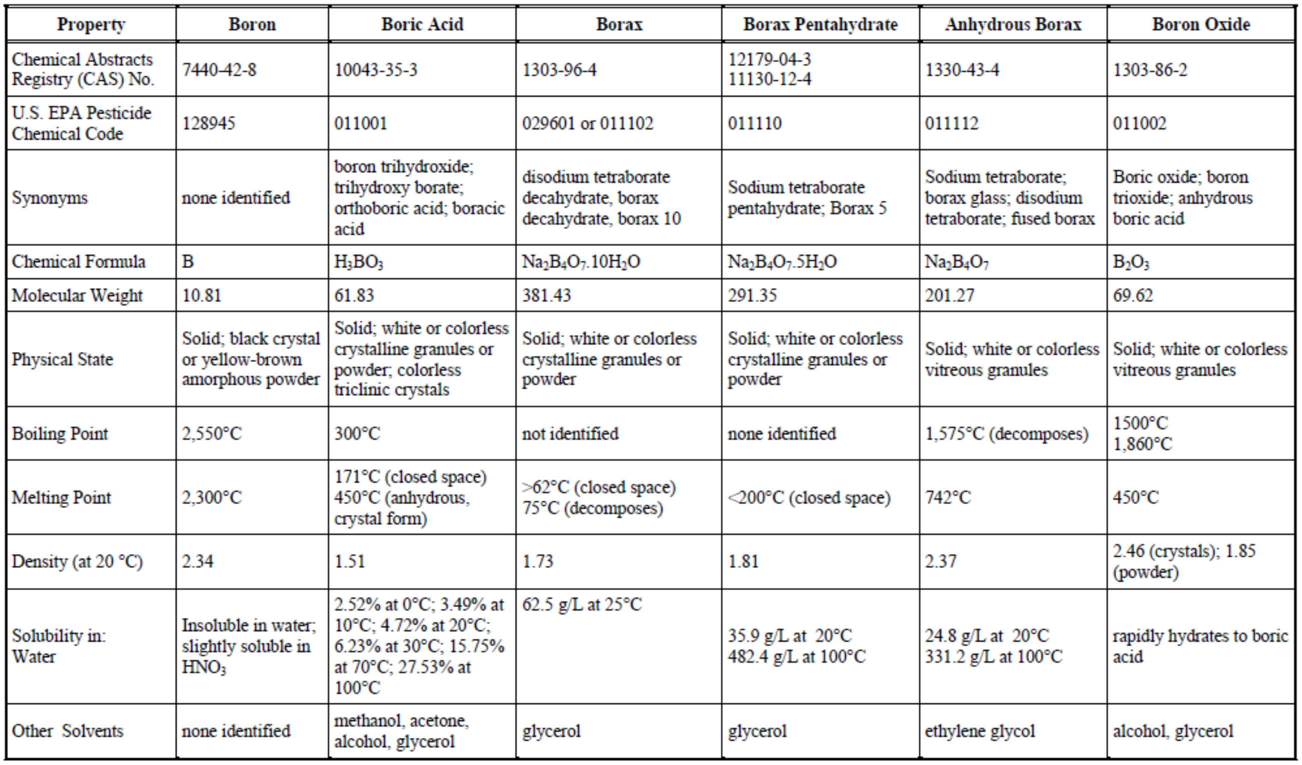
[1] Environmental Protection Agency

Table 1. Chemical and physical properties of boron and related compounds adapted from EPA[4]



Property	Boron	Boric Acid	Borax	Borax Pentahydrate	Anhydrous Borax	Boron Oxide
Chemical Abstracts Registry (CAS) No.	7440-42-8	10043-35-3	1303-96-4	12179-04-3 11130-12-4	1330-43-4	1303-86-2
U.S. EPA Pesticide Chemical Code	128945	011001	029601 or 011102	011110	011112	011002
Synonyms	none identified	boron trihydroxide; trihydroxy borate; orthoboric acid; boracic acid	disodium tetraborate decahydrate, borax decahydrate, borax 10	Sodium tetraborate pentahydrate; Borax 5	Sodium tetraborate; borax glass; disodium tetraborate; fused borax	Boric oxide; boron trioxide; anhydrous boric acid
Chemical Formula	B	H_3BO_3	$Na_2B_4O_7.10H_2O$	$Na_2B_4O_7.5H_2O$	$Na_2B_4O_7$	B_2O_3
Molecular Weight	10.81	61.83	381.43	291.35	201.27	69.62
Physical State	Solid; black crystal or yellow-brown amorphous powder	Solid; white or colorless crystalline granules or powder; colorless triclinic crystals	Solid; white or colorless crystalline granules or powder	Solid; white or colorless crystalline granules or powder	Solid; white or colorless vitreous granules	Solid; white or colorless vitreous granules
Boiling Point	2,550°C	300°C	not identified	none identified	1,575°C (decomposes)	1500°C 1,860°C
Melting Point	2,300°C	171°C (closed space) 450°C (anhydrous, crystal form)	>62°C (closed space) 75°C (decomposes)	<200°C (closed space)	742°C	450°C
Density (at 20 °C)	2.34	1.51	1.73	1.81	2.37	2.46 (crystals); 1.85 (powder)
Solubility in: Water	Insoluble in water; slightly soluble in HNO_3	2.52% at 0°C; 3.49% at 10°C; 4.72% at 20°C; 6.23% at 30°C; 15.75% at 70°C; 27.53% at 100°C	62.5 g/L at 25°C	35.9 g/L at 20°C 482.4 g/L at 100°C	24.8 g/L at 20°C 331.2 g/L at 100°C	rapidly hydrates to boric acid
Other Solvents	none identified	methanol, acetone, alcohol, glycerol	glycerol	glycerol	ethylene glycol	alcohol, glycerol

Boron can be found in surface water and groundwater, the latter is highly affected by wastewater discharges. Based on WHO[2] guidelines, boron concentration in groundwater varies from less than 0.3 to more than 100 mg L^{-1} throughout the world[7]. This guideline also called for a provisional boron concentration of 0.5 mg L^{-1} for drinking water[7] which was elevated to 2.4 mg L^{-1} later in 2011[8]. Boron can contaminate water bodies as a result of natural processes or human activities and can vary in concentration in surface water, runoff or wastewater[9]. The most common reason for the presence of boron in the wastewater is the application of boron compounds as a bleaching agent in detergents and cleaning products. Due to the toxicity of a high concentration of boron, different standards limited its concentration in drinking water, irrigation water and wastewater; however those limits vary in different regions. California state

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[2] World Health Organization

guideline recommended 1 mg boron per liter of drinking water while the EPA suggested that non-regulatory concentrations of boron in drinking water should be about 5 mg/L. The EPA study declares that at this concentration adverse health effects are not anticipated to occur in adults over long term exposure, assuming that human daily water consumption is about 2 L/ day[5]. The California Department of Public Health (CDPH) also regulates boron as one of drinking water contaminants. The current Notification Level (NL) for boron, proposed by CDPH, is 1,000 µg/L (1 mg/L) [10].

Boron is also present in seawater, mainly in a form of boric acid in low level. Boron concentration in seawater is estimated to be around 4-5 mg L^{-1} which exceeds allowable level of boron for irrigation application of seawater [11, 12]. Although, boron is a necessary element for plant growth and must be provided through irrigation or fertilizer, it can become fairly toxic at higher concentrations for different species. At a normal concentration, effects of boron on mammals, birds and fish are negligible; nonetheless it is toxic to insects which makes boron an ideal choice for a use as insecticides[6].

Commercial boron compounds are widely employed in manufacturing industries such as glass industry for the production of optic and chemically stable glass, enamels, cosmetic, leather, detergents, insecticides and in the preparation of disinfectants and drugs[4, 13].

3. Literature Review

3.1. Chemical properties of boron

Boron chemistry is unique and complex since its chemical and physical properties are significantly different from the other elements in its group. Except for high reducing power, boron shares only few similarities with neighboring elements in the periodic table [12, 14, 15]. Elemental boron is rare and its difficult preparation procedure imposes constraints on experimental and theoretical study of boron chemistry. Researchers and chemists acknowledge that boron chemistry has reached state of sophistication rather than maturity that represents its many- faceted chemistry.

Boron is a low-abundance element in the Earth's crust that occurs as trace element in most soils[16, 17]. Two forms of elementary boron are recognized as 1) fine crystalline (amorphous boron) which is brown in color and 2) crystalline boron of dark grey color. Two crystalline structures of boron, namely, α-rhombohedral boron (Figure. 1) and β-rhombohedral boron (Figure. 2) exist at atmospheric pressure[18]. According to Table 2, boron is distributed in various component of the Earth[4].

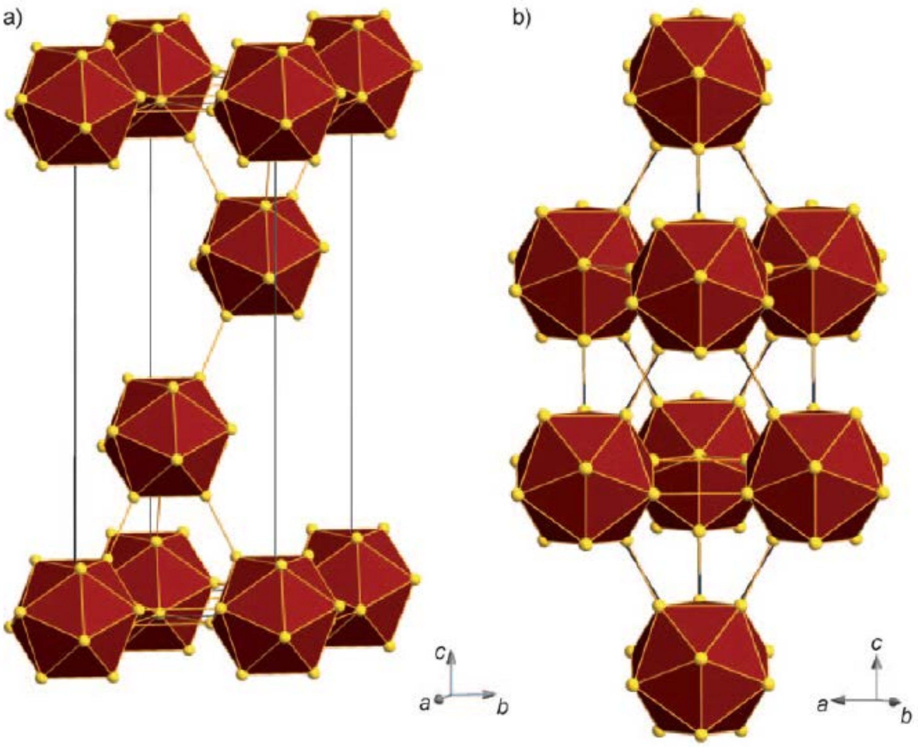


Figure 1. Unit cells of α-boron. (a) Hexagonal setting and (b) rhombohedral setting

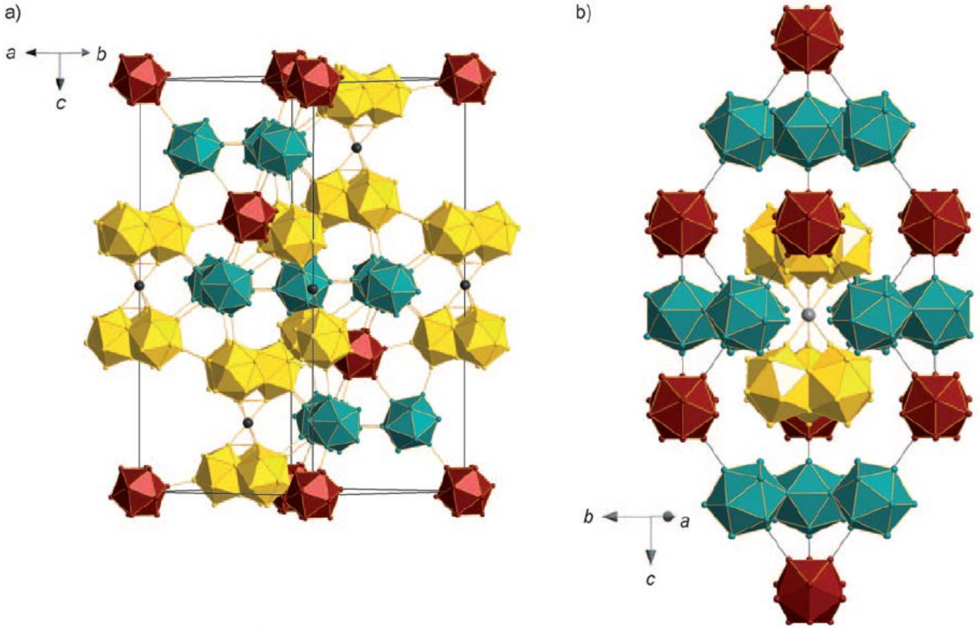


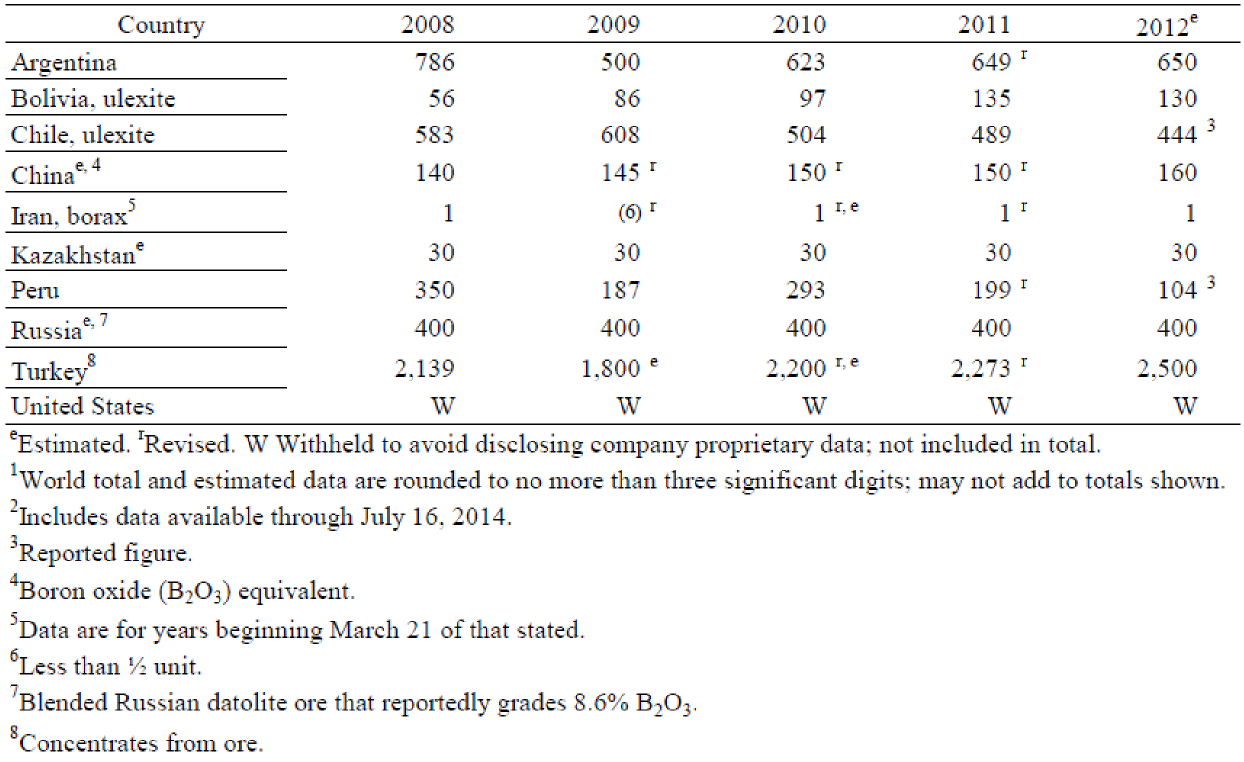
Figure 2. Unit cells of β-boron. (a) Hexagonal setting and (b) rhombohedral setting

Table 2. Distribution of Boron in the Earth' components

Source	Weight percent of boron
Earth’s crust	$1 * 10^{-3}$
Sedimentary rocks	$1.2 * 10^{-3}$
soils	$1 * 10^{-3}$
Marine clays	$5 * 10^{-3}$
Sea water (dry residue)	$1.5 * 10^{-3}$
Salt springs (dry residue)	$(3\text{-}20) * 10^{-3}$
Marine plants (ash)	$1.5 * 10^{-3}$
Marine animals (ash)	$(3\text{-}100) * 10^{-3}$
Clover, alfalfa (dry matter)	$(7\text{-}57) * 10^{-3}$

Although boron compounds are widespread in nature, its naturally occurring minerals are to be found only in few locations. Boron accumulated in rich borate bed in arid regions such as California as a result of evaporation of water containing boric acid. Large deposits of boron minerals are available in the area of former volcanic activity or thermal activity such as hot springs[16, 17]. The largest borate deposits are located in the Mojave Desert of the United States, the Alpide belt in southern Asia, and the Andean belt of South America. Table 3 represents the major countries in producing boron[19]. In both 2011 and 2010, California was the only producer of boron in the Nation. Boron was California’s second most valuable mineral commodity in terms of dollar value, after construction sand and gravel in 2011[20].

Table 3. Boron minerals: world production, by country [1, 2] (Thousand metric tons)



Country	2008	2009	2010	2011	2012[e]
Argentina	786	500	623	649 [r]	650
Bolivia, ulexite	56	86	97	135	130
Chile, ulexite	583	608	504	489	444 [3]
China[e, 4]	140	145 [r]	150 [r]	150 [r]	160
Iran, borax[5]	1	(6) [r]	1 [r, e]	1 [r]	1
Kazakhstan[e]	30	30	30	30	30
Peru	350	187	293	199 [r]	104 [3]
Russia[e, 7]	400	400	400	400	400
Turkey[8]	2,139	1,800 [e]	2,200 [r, e]	2,273 [r]	2,500
United States	W	W	W	W	W

[e] Estimated. [r] Revised. W Withheld to avoid disclosing company proprietary data; not included in total.

[1] World total and estimated data are rounded to no more than three significant digits; may not add to totals shown.

[2] Includes data available through July 16, 2014.

[3] Reported figure.

[4] Boron oxide (B_2O_3) equivalent.

[5] Data are for years beginning March 21 of that stated.

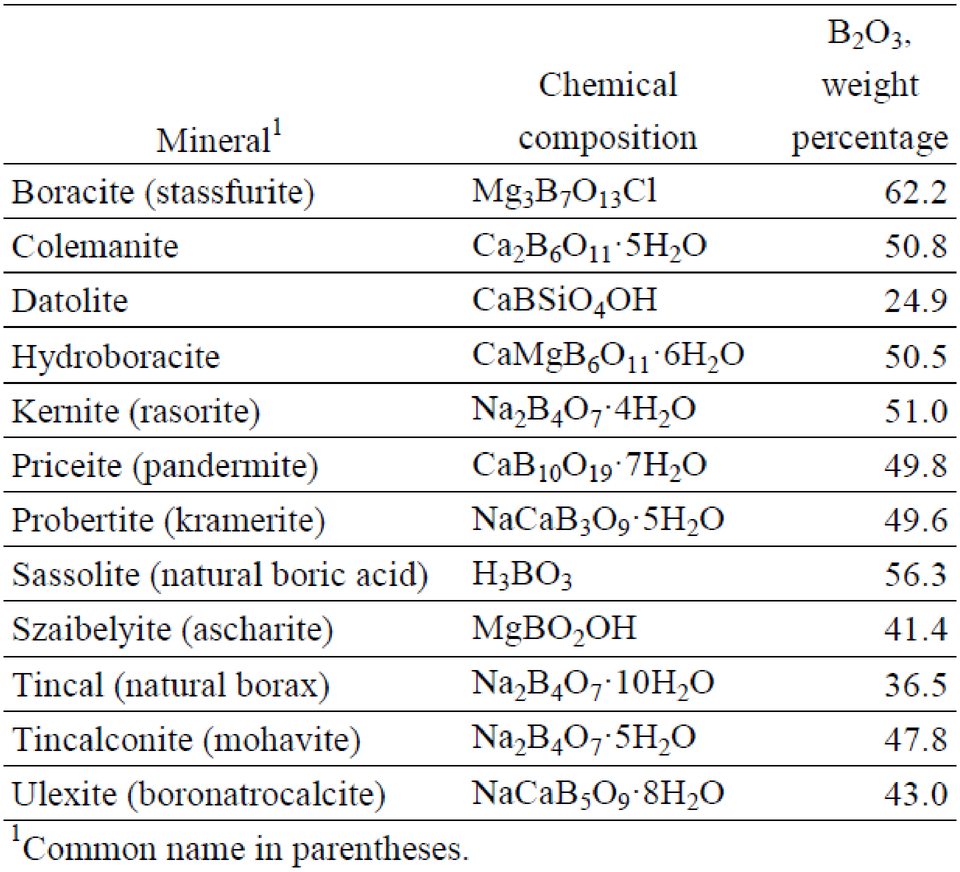
[6] Less than ½ unit.

[7] Blended Russian datolite ore that reportedly grades 8.6% B_2O_3.

[8] Concentrates from ore.

Four principal commercially valuable boron ores in the United States are: sodium borates tincal, kernite, the calcium borate colemanite, and the sodium-calcium borate ulexite[21]. Boron products are priced and sold based on boric oxide content (B_2O_3), which varies by ore and compound, and on the absence or presence of sodium and calcium (Table 4) [19].

Table 4. Boron minerals of commercial importance



Mineral[1]	Chemical composition	B_2O_3, weight percentage
Boracite (stassfurite)	$Mg_3B_7O_{13}Cl$	62.2
Colemanite	$Ca_2B_6O_{11}\cdot 5H_2O$	50.8
Datolite	$CaBSiO_4OH$	24.9
Hydroboracite	$CaMgB_6O_{11}\cdot 6H_2O$	50.5
Kernite (rasorite)	$Na_2B_4O_7\cdot 4H_2O$	51.0
Priceite (pandermite)	$CaB_{10}O_{19}\cdot 7H_2O$	49.8
Probertite (kramerite)	$NaCaB_3O_9\cdot 5H_2O$	49.6
Sassolite (natural boric acid)	H_3BO_3	56.3
Szaibelyite (ascharite)	$MgBO_2OH$	41.4
Tincal (natural borax)	$Na_2B_4O_7\cdot 10H_2O$	36.5
Tincalconite (mohavite)	$Na_2B_4O_7\cdot 5H_2O$	47.8
Ulexite (boronatrocalcite)	$NaCaB_5O_9\cdot 8H_2O$	43.0

[1] Common name in parentheses.

As mentioned before, boron is in the Group 13 of periodic table and the ground state configuration is $1S^2\ 2S^2\ 2P^1$. This configuration would be a chemistry of monovalent boron, however exited electron configuration of boron is $1S^2\ 2S^1\ 2P^2$. According to latest configuration, boron is trivalent in most cases and the oxidation state is +3[4, 17]. Boron also thought to be electron deficient since three single bond would not support stable electron configuration. Therefor born has strong tendency to form stable covalent bonds with electronegative atoms such as oxygen. In fact naturally occurring boron is found exclusively bound to oxygen as borates[22]. Electron deficiency of boron is what accounts for boron being a strong Lewis acid, in that it can accept protons (H^+ ions) in solution[14]. Boron also uses hydrogen atoms to bridge between two boron atoms or rarely forms boron-boron bound to compensate electron deficiency[17].

Among all boron compounds and minerals, H_3BO_3 hereafter boric acid and $Na_2B_4O_710H_2O$, borax, fall within the scope of this research since they are incorporated into laundry detergents, soaps, and other cleaning products.

3.1.1. Boric acid

Two forms of boric acid in free state are: metaboric acid, HBO_2, and orthoboric acid H_3BO_3. Orthoboric acid, or simply boric acid is obtained from mineral sassolite and crystallizes in the form of fine, waxy and white flakes. Crystalline boric acid is essentially layers of H_3BO_3 molecules held together by hydrogen bonds[23]. Some of important physicochemical properties of boric acid are given in Table 5[4, 24].

Table 5. Physicochemical properties of boric acid

Property	Unit	Numerical value
Density	g/cm^3	1.48-1.51
Heat of dehydration (to form crystalline orthoboric acid)	kcal/mole of boric acid	-9.3(25^o)
Heat of vaporization	kcal/mole of boric acid	23.43
Heat of solution (to form a 0.05M solution)	kcal/mole of boric acid	-5.166

When boric acid is heated, it loses water, changing to three different crystal forms of metaboric acid. Upon more heating at high temperature, composition of a viscous liquid containing HBO_2 and B_2O_3 has been observed[24, 25]. Figure 3 demonstrates the dehydration diagram and melting point for the H_2O-B_2O_3 system.

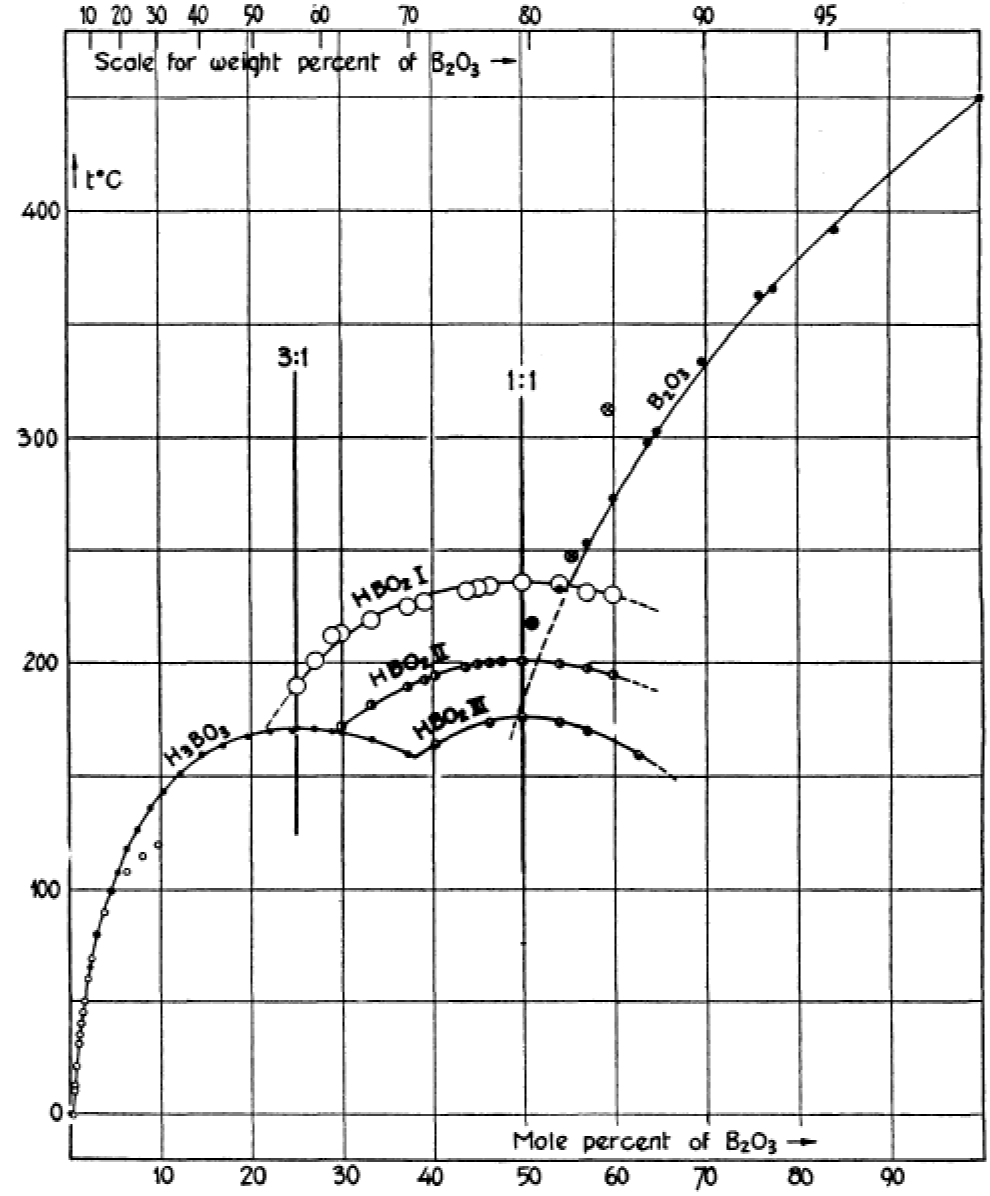


Figure 3. Dehydration diagram for the H_2O-B_2O_3 system

Following equations describe dehydration process of boric acid[23]:

Orthoboric acid gradually loses water, and changes to metaboric acid

$$H_3BO_3 \longrightarrow HBO_2 + H_2O$$

At higher temperatures, all the water is lost, and anhydrous boric oxide is formed

$$2H_3BO_3 \longrightarrow B_2O_3 + 3H_2O$$

In water, boric acid exists in monomeric form of $B(OH)_3$ in which boron and oxygen atoms form a planner arrangement. Therefor the aqueous boric acid molecules formula can be described as $^{-}B(OH)_3(^{+}OH_2)$ that explains its monomeric, uncharged and weak Lewis acid nature[4, 24, 26]. The solubility of boric acid as well as other boron compounds is illustrated in figure 4[27]. Borate arrangement in borax, including more bonds between ions, accounts for greater stability of borax against dehydration[28].

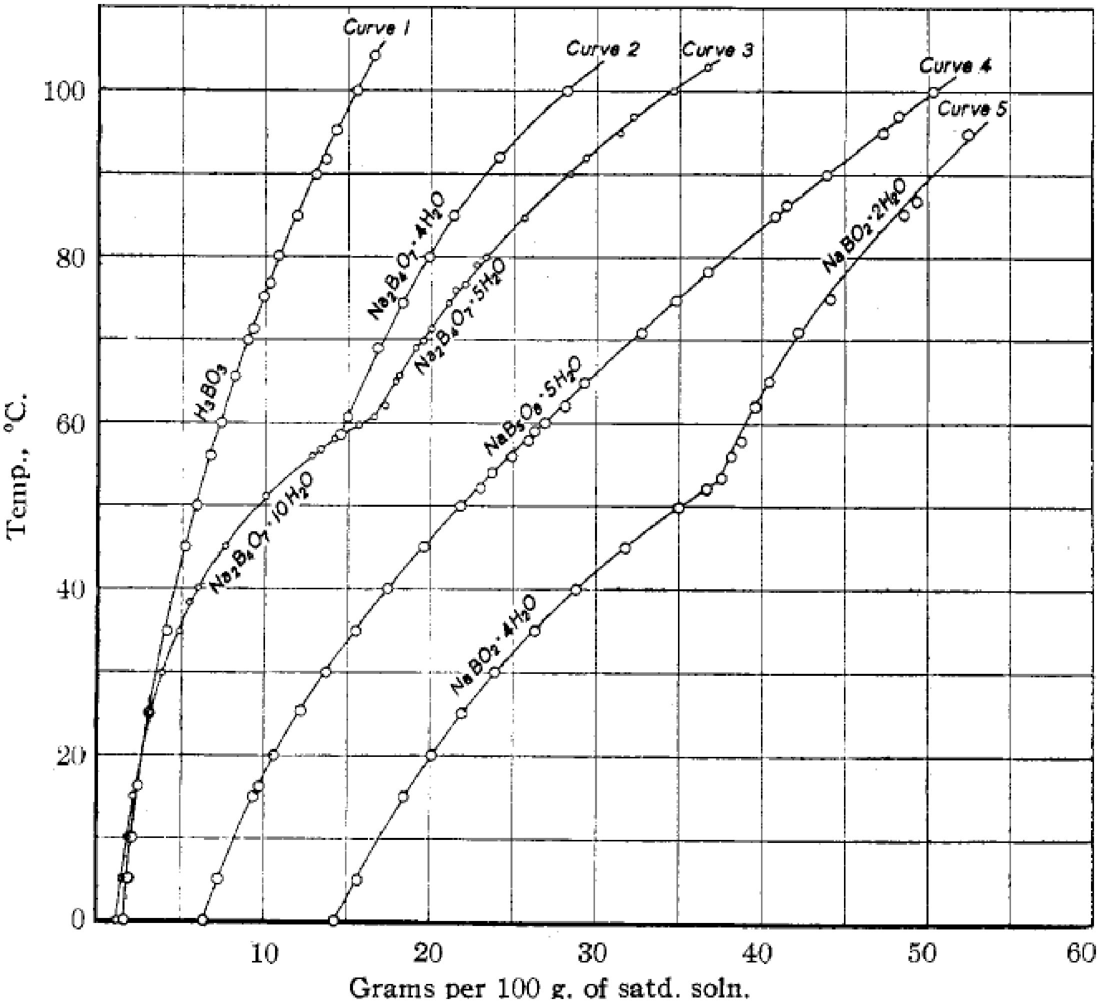


Figure 4. Solubility diagram of boric acid and other boron compounds

Boric acid is a weak acid with the first dissociation constant of $5*10^{-5}$. However, the acidic properties of boric acid increase in presence of some natural salts.

The boric acid ion is hydrated in aqueous solution according to following reaction[4, 26]:

$$H_3BO_3 + 2H_2O \longleftrightarrow H_3O^+ + B(OH)^-{}_4$$

Based on this equation boric acid accepts hydroxide ion from water and releases a proton into solution. Boric acid dissociates as a function of pH. At higher pH, the anion, $B(OH)_4{}^-$, is predominant, while at lower pH the uncharged species are predominant. At low concentrations (≤0.02M), only the mononuclear species $B(OH)_3$ and $B(OH)^-{}_4$ are present. At higher concentrations and with increasing pH, polynuclear ions such as $B_2O(OH)_6{}^{2-}$ or those incorporating B_3O_3 rings such as $B_3O_3(OH)^-{}_4$ are formed. Thus, at the higher concentration, the interaction between $B(OH)_3$ and $B(OH)^-{}_4$ may occur based on following equation[22]:

$$B(OH)_3 + 2B(OH)_4^- \longleftrightarrow [B_3O_3\,(OH)_5]^{2-} + 3H_2O$$

Formation of other polymeric species is feasible based on following equation[29]:

$$3\,B(OH)_3 = B_3O_3(OH)_4^- + H^+ + 2H_2O \quad pK=6.84$$

3.1.2. Borax

Sodium borates as shown in table 6, in their 5- and 10- hydrate and anhydrous forms are commercially the most important compounds of borate[24]. 10-hydrate form of sodium borate is incorporated in many cleaning and personal care products, metallurgical fluxes, corrosion inhibition, adhesives, wire drawing and stabilizers.

Table 6. Molecular formula of sodium borate compounds[30]

Name of compound Property	Anhydrous borax	Borax pentahydrate	Borax (Sodium tetraborate decahydrate)
Molecular formula	$Na_2B_4O_7$	$Na_2B_4O_7.5H_2O$	$Na_2B_4O_7.10\ H_2O$
Molecular weight	201.27	291.35	381.43
Boron content (%)	21.49	14.85	11.34

The early use of sodium tetraborate decahydrate, $Na_2BO_4.10H_2O$, or borax was to make perborate, the bleaching agent used in household detergent[30]. It can contribute to the softening of hard water by tying up calcium ions, as well as acting as a buffer agent. Sodium perborates such as $NaBO_3$ $.1H_2O$ or $4H_2O$ have been added into powdered detergents. Perborates release hydroperoxide ion upon their dilution in alkaline wash water based on following equation[21] :

$$Na_2\,[(HO)_2B(OO)_2B(OH)_2\,] * 6H_2O + 2OH^- \longrightarrow 2NaB(OH)_4 + 2OOH^- + 4H_2O$$

Borax also can be converted to boric acid by the action of hydrochloric acid[31]:

$$Na_2B_4O_7 * 10H_2O + 2\ HCl \longrightarrow 4\ H_3BO_3\,[\text{or } B(OH)_3] + 2\ NaCl + 5\ H_2O$$

3.2. Boron impact on plants

Boron is an essential element for plant growth and it can be added directly to the soil as fertilizer[13], though high concentrations of boron are toxic to plants. Therefore it is important to quantify the minimum and maximum concentrations of boron for proper growth of plants.

Boron can support the growth of plants and crops in different processes. One such process is the ability of boron to facilitate sugar movement from leaves to stems. Gauch and Dugger ‘s 1953 study demonstrated that boron deficiency symptoms correlate with sugar deficiency as sugar accumulates in leaves and cannot move towards other parts of the plant[32]. Boron also plays a role in the growth of the cell wall. Brown et al. reported the importance of sufficient boron in the stabilization of cell wall as well as the regulation of pore sizes[33]. Sprague summarized that boron is involved in other aspects of plant growth such as enzymatic reactions, nucleic acid metabolism along with cell structure[6].

While the requirement of plants for boron is well established, high concentrations of boron in irrigation water can lead to damage of some plants and crops. Accumulation of boron in leaves and roots of plants due to transpiration induces boron toxicity. Toxicity symptoms appear on older leaves as a yellowing, spotting, or drying of leaf tissue at the tips and edges.

A plant tolerance to boron is one of the most important criteria for greywater treatment and it is critical to adjust and develop greywater treatment processes in order to avoid generating plant toxicity. One must to take into account that soil structure, pH, rainfall and humidity are also play a role in overall boron uptake by plants.

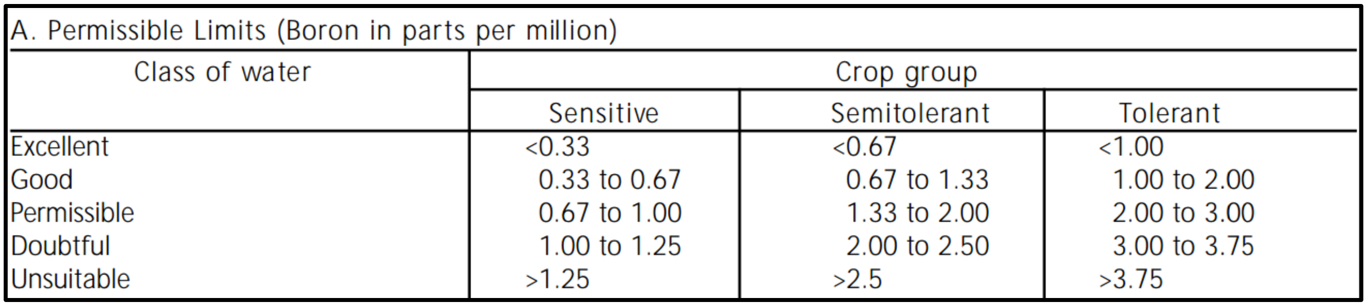
Not all crops are equally sensitive to boron; some plants can show boron deficiency at a concentration that would be toxic to other. The first extensive, quantitative comparison of the effect of boron on fifty species of plants was that of Eaton who used sand culture for plant growth and irrigated them with different boron concentrations in standard nutrient solution. Table 7 which is developed based on Eaton’s measurements contains boron concentrations for best growth and the lowest concentration for toxicity. According to Table 7, plants are classified as sensitive if they have tolerance index of less than 50, semi tolerant for plants with indexes of 50-100 or tolerant for an index greater than 100. The index is 100 times the ratio of the average weight of plants grown in 5, 10, and 15 ppm boron to the largest weight of plants grown in either trace or 1 ppm boron in solution[34].

Table 7. Plants growth as affected by plant (Adapted from Eaton, 1944)

Plant	Boron concentration for best growth ppm	Lowest concentration for injury ppm	Relative tolerance
Sensitive			
Violet	Trace	5	20
Grape	1	5	9
Pansy	Trace	5	24
Semi tolerant			
Pea	1	5	55
Sweet potato	Trace	5	63
Celery	15	25	89
Alfa alfa	15	15	98
Tolerant			
Turnip	5	25	115
Cotton	10	10	130
Asparagus	15	25	217

Crop sensitivity is the limiting factor for boron concentration in irrigation water. There are different guidelines that define permissible limit of boron in irrigation water. Rowe and Abdel-Magid summarized detailed guidelines for allowable concentration of boron in reclaimed water intended for agricultural reuse. Their result is presented in Table 8[1].

Table 8. Limits of boron in irrigation water[1]



A. Permissible Limits (Boron in parts per million)

Class of water	Crop group		
	Sensitive	Semitolerant	Tolerant
Excellent	<0.33	<0.67	<1.00
Good	0.33 to 0.67	0.67 to 1.33	1.00 to 2.00
Permissible	0.67 to 1.00	1.33 to 2.00	2.00 to 3.00
Doubtful	1.00 to 1.25	2.00 to 2.50	3.00 to 3.75
Unsuitable	>1.25	>2.5	>3.75

3.3. Survey of boron in products

Boron compounds have many applications worldwide. The principal industrial uses of borax and boric acid are in the production of glass, ceramics, soaps, detergents, and bleaches. Figure 5 illustrates the U. S. consumption of boron compounds by end use.

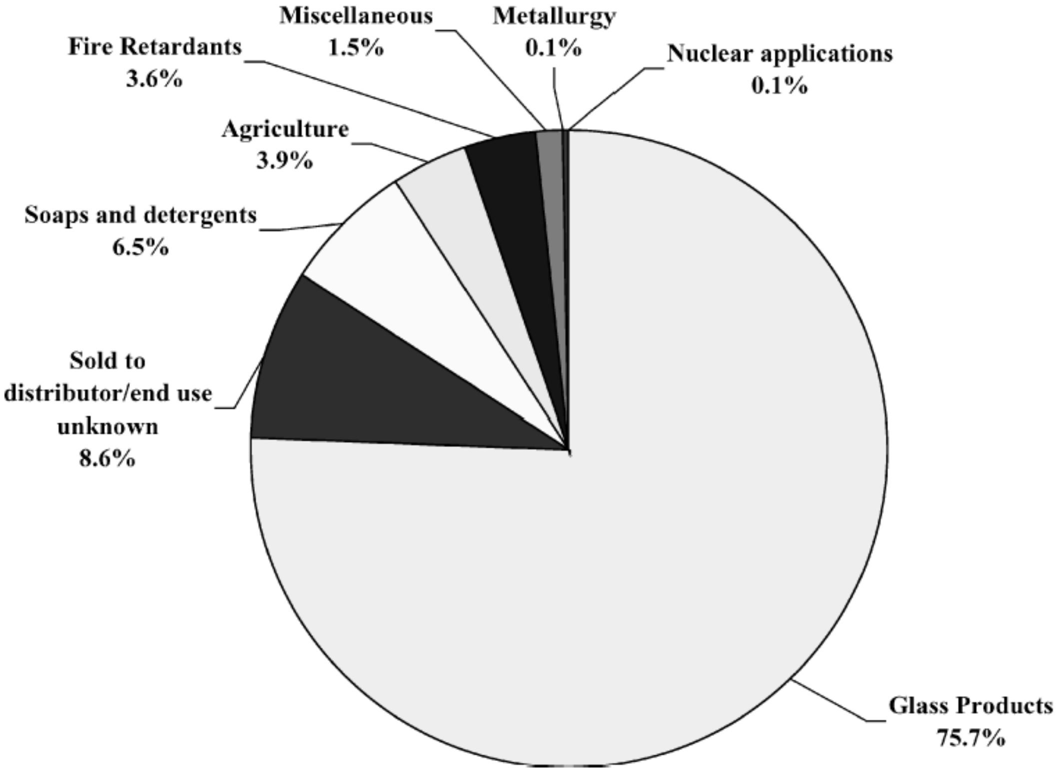


Figure 5. Year 2000 U.S. consumption of boron by end use[14]

Boron is used as an additive in glass production because of its mechanical properties. Boron can reduce thermal expansion of glass and therefor improving its strength, chemical resistance, and durability. It also can provide resistance against vibration, high temperature, and thermal shock.

Boron also can improve manufacturing of glass by reducing the viscosity of glass during production [14, 19]. Depending on the application and quality of the glass, borax, boric acid, colemanite, ulexite, and sodium borates can be used[19].

Boron compounds offer benefits in detergency so they can be used in the manufacturing of detergents and bleaches as well. Some of those benefits are as following:

- Alkaline buffering and pH control of solution
- Borate and perborates form soluble complexes with the calcium ion. As a result water hardness is reduced upon removal of calcium ions.
- Improvement of surfactant performance. Negative surfactants can form complexes with calcium ion in water prior to delivering their detergency function. Borates compete successfully with the surfactant for the calcium ions and formation of complexes between them improves surfactant performance.
- The borate component aids overall detergency

Boron is added to detergents in the form of sodium perborates or perborate tetrahydrate since they have a peroxygen bonds that can deliver oxidizing bleaching agent to solutions. Sodium perborate, however, requires hot water (60^oC) to undergo hydrolysis, unless an activator is present. Concerns have emerged over excessive boron levels in wastwater due to sodium perborate in detergents. Sodium percarbonate has been used as a substitute primarily in Europe because it produces hydrogen peroxide at lower temperatures. This substitution has affected boron consumption [14, 19].

U. S. department of health and human service provides a database about chemical ingredients of over 14000 consumer brands. Available information is from brand-specific labels and Material Safety Data Sheets provided by manufacturers.

Following table is adapted from U. S. department of health and human service website and indicates the percentage of different boron compounds in various household products[35].

Table 9. Percentage of boron compounds in different cleaning products

Brand	Form	Percent
Sodium tetraborate anhydrous **$Na_2B_4O_7$**		
Cheer Liquid Laundry Detergent-01/08/2004-Old Product	Liquid	1-5
Tide Ultra Liquid-03/24/2006	Liquid	1-5
Tide Free Ultra Liquid-03/24/2006	Liquid	1-5
Gain Liquid Detergent, Original	Liquid	0.5-5
Era Liquid Laundry Detergent-01/11/2008	Liquid	1-5
Sodium tetraborate pentahydrate **$Na_2B_4O_7.\ 5H_2O$**		
Whink Wash Away Pre-Treatment & Stain Remover	Liquid	1-4
Whink Uniform Wash, Laundry Stain Remover	Liquid	0.5-1.5
Sodium borate decahydrate **$Na_2B_4O_7.\ 10H_2O$**		
Ivory Snow Liquid Laundry Detergent-Old Product	Liquid	1-5
Spray N Wash Stain Stick-04/11/2002-Old Product	Solid	1-2
Seventh Generation, Natural Lavender Laundry Liquid	Liquid	0.03-3
Seventh Generation, Sensitive Care Laundry Liquid	Liquid	1-10
DIP-IT Food & Beverage Stain Cleaner Powder-01/08/2010	Powder	2.5-10
OxiClean Max Force 4 In 1 Stain Fighting Power Pre-Treater Gel Stick	Solid	1-2
Boraxo Powdered Hand Soap-08/30/2007-Old Product	Powder	60-100

Twenty Mule Team Powdered Hand Soap-08/30/2007-Old Product	Powder	60-100
Boric acid **H_3BO_3**		
Hot Shot Maxattrax Ultra Brand Ant Killing Gel	Gel	5
Cascade Automatic Dishwashing Liquigel-09/07/2006	Gel	1-5
Green Works Natural Laundry Stain Remover	Liquid	1-5
Seventh Generation Baby Natural 4X Laundry Detergent, Fresh & Clean	Liquid	1-3

4. Boron removal technologies

Numerous of technologies have been proposed for boron removal. This paper attempts to review conventional and advanced methods for boron removal. Most boron removal processes developed around the idea of using seawater or contaminated water as a source of potable or irrigation water since nearly all of those water sources have concentrations of boron which usually exceed allowable limits.

4.1. Chemical precipitation

Among different technologies, chemical precipitation is well-adapted for removal of boron at high concentrations. Some chemical precipitation reactions have the ability to utilize different precipitants to remove boron. Xu and Jiang mentioned the potential of organic and inorganic compounds to precipitate boron from a solution through the coagulation-precipitation processes[13]. They also extensively reviewed application and effectiveness of those compounds. Table 10 is adapted from their review and shows chemical precipitants for boron removal.

Table 10. Common chemical precipitant for boron removal(Adapted from Xu and Jiang, 2008)[13]

Precipitant	Sample	Initial concentration	Final concentration	Favorable conditions	Limitation
Inorganic precipitant					
Lime	2.65:1 as mole ratio of B:Ca, in boric acid solution	6200 mg/L (B) .	450 mg/L (B) 400-600 mg/L (Ca)	pH=10 1-4 days 25 °C	Dependent on pH, reaction time, relative concentration More removal(400 mg/L) is possible by adding more lime (high pH and significant quantity of lime)
Powdered lime	50 g/L of powdered lime	700 mg/L (B)	50 mg/ (B)	90 °C 2 h	
aluminum sulfate	1125 mg/L with lime for incinerator quench water	1.2 mg/L	0.16 mg/L(87%)	pH =12.0	
Iron salts	sequential addition of		10 mg/L	pH 8-9	Iron(III) is better since

	reagent.				iron(II) precipitates were difficult to filter
Magnesium oxide			95% removal	10 h at 20 ^{o}C possible to use water to remove B2O3 from the metal oxide after heat treatment	Dependent on quality of reagent and contact time
Alumina-Lime-Soda Process	Raw water	1.7 mg/L	0.2 mg/L	Method for softening brackish water	
Organic precipitant					
Polyvinyl Alcohol (PVA).		150 mg/L	60% removal	room temperatur, additional calcium hydroxide improves removal	
Hydroxycarboxylic Acid				Formation of complex	Dependent on number of groups (hydrous or carboxylic), pH,concentration and precipitation mode

Organic Dioxime	1,2-cyclohexanedione dioxime (nioxime)	1000 mg/L			High cost

Remy et al indicated the difficulty of quantifying boron precipitation from dilute solution and expensive process of drying final solution to acquire final product. They proposed the novel method by using calcium hydroxide in powder form and they successfully reduced the concentration of boron from 700 to less than 50 mg L^{-1} by maintaining high temperature about 90^{o} C for about 2 hours[9].

Although different precipitants are capable of removing boron form water, the effective chemical precipitation requires adjusting water pH and high chemical doses and other assistant coagulants are required for removing boron from low concentration solution. Voluminous amount of sludge as a result of chemical reaction is another issue associated with this method[13].

4.2. Ion exchange

In the study done by Aly et al, boron was determined in olive mill waste water with the concentration of 9.8 mg L^{-1}, using the azomethine-H method. Proposed method is basically based on three successive columns treatment including columns of gravel, sand and natural zeolite as an ion exchanger. They found that the zeolite is an efficient treatment and can decrease concentration of boron by 92.4% to 0.74 mg L^{-1}. Figure 6 illustrates effectiveness of zeolite in reducing boron from olive mill wastewater and also indicates that latter processes are not capable of reducing more boron from solution[36].

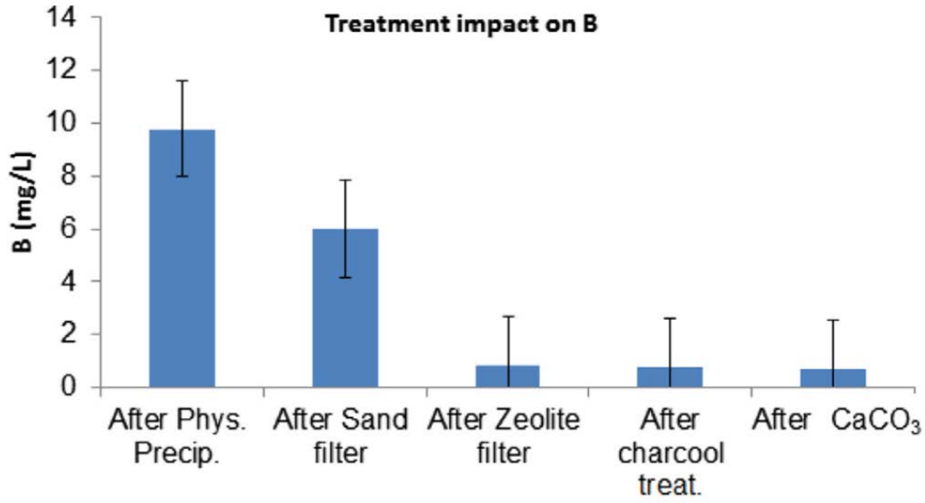


Figure 6. Impact of different treatment steps on boron removal from olive mill wastewater

4.3. Adsorption

In general sorption process is one of the most promising methods to remove contaminants from water due to low waste generation, moderate cost and possibility of using natural material as adsorbent. Adsorption processes are frequently used in water treatment to remove synthetic organic chemicals, disinfection by products as well as taste and odor[37], while adsorption treatment of wastewater is supplementary process in addition to conventional biological processes for the removal of refractory constituents and heavy metals[38].

Activated carbon which has porous structure on its surface is formed by thermochemical decomposition of organic materials followed with exposure to oxidizing gases[38]. Although activated carbon is one of the principal types of adsorbents, it does not demonstrate a high ability for boron removal[13] [39]. In the experiment that was originally designed for investigating effectiveness of different adsorbents within static and dynamic flow, effect of different impregnantes was also reported. It was found that application of different impregnantes can increase boron adsorption by activated carbon. Among those experiments, removal of boron using activated carbon impregnated with mannitol exhibited more efficiency[39].

In another experiment, boron removal from high and low concentrated aqueous solutions was investigated by using activated alumina. Bouguerra et al demonstrated that 0.8 and 5 g of activated alumina are capable of up taking 40% and 65% of boron from low and high boron concentration solutions respectively. According to their batch experiment, optimal stirring time is about 30 minute and pH should be kept around 8.5 for both concentration of 5 and 50 mg L^{-1} of boron in solution[40].

Fly ash is also reported to have the potential of being adsorbent for removal of contaminants. One advantages of fly ash over activated carbon is the fact that fly ash is waste product of combustion, therefor it is cheaper and there is no need of regeneration after utilization which again can reduce the total cost. Ozturk and Kavak examined the effectiveness of fine particle size of fly ash (250-400µm) for removing boron at the concentration of 600 mg $L^{-1}$from H_3BO_3 solution in batch and column adsorption experiments. They also investigated the effect of pH, agitation time, initial boron concentration, temperature and adsorbent dosage in the final boron removal. In all experiments, boron removal tended to decline with increasing temperature, and the 90% removal were observed at 25^o C and pH of 2 by using 4-5 gram of fly ash in 50 mL solution (figure 7). Column experiment revealed higher capacity of adsorption about 46.2 mg / g compare to adsorption capacity of 20.9 mg/ g for batch experiment[41].

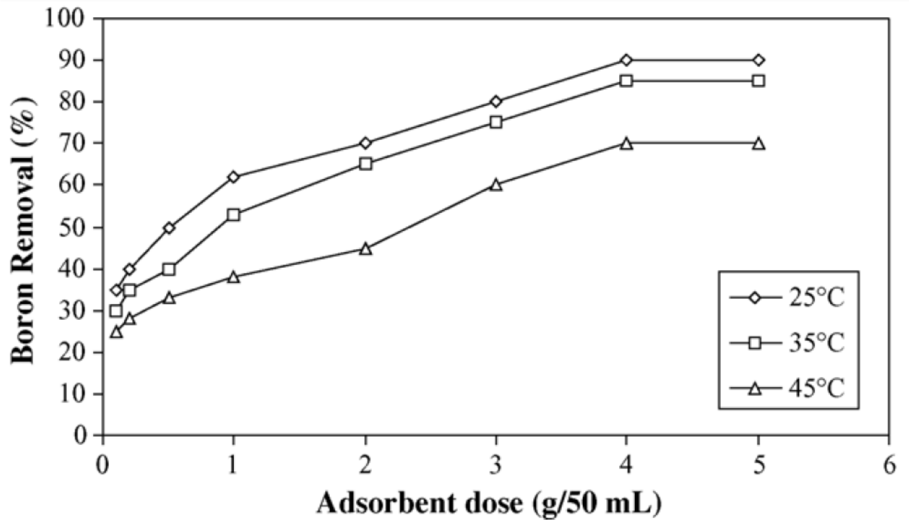


Figure 7. Effect of adsorbent dose on the removal of boron at pH=2[41]

Elsewhere, capability of crushed coal and three different fly ash samples obtained from different power plants to boron removal from sea water and desalinized seawater were examined. Polat et al demonstrated that one type of flay ash is able to reduce boron level from sea water by 97% while lowest removal was observed to be 60%, using crushed coal. However, coal is a better candidate for continuous treatment since it can maintain its specification after several regeneration cycles. They also conducted various batch and column experiments and found that boron removal efficiency depends to some extent on reaction time and liquid to solid ratio[42]. Other unconventional adsorbents also acquire the ability of adsorbing boron. Red mud is an example of such a low cost material, which is a waste residue from alumina refineries. It can be used as a mixed adsorbent with different metal oxides. Cengeloglu et al found that neutralized red mud can remove about 93% of boron from solutions which initial concentration of boron is 43 mg L^{-1}. They also observed that in batch equilibration technique the equilibrium time needed for adsorption is about 20 minutes which is relatively shorter compare to other adsorbents[43].

4.4. Reserve osmosis

Reserve osmosis as a continuous separation, utilizes membrane property to separate dissolved solute from water. Water has to be pressurized towards semipermeable membrane to overcome natural osmotic pressure[37]. RO[3] is widely used for desalination of seawater or brackish water especially for irrigation purposes in area where the shortage of water is a concern. In wastewater treatment, RO is considered as a highly effective treatment to remove remaining dissolved constituents after advance treatment. However, high efficiency is achieved only if a high quality of feed water is introduced to RO unit[38].

Boron is present in seawater at the concentration of 4 to 5 ppm[11]. Boron in seawater is found in form of boric acid, H_3BO_3, weak acid that has poor rejection in its neutral form. Higher rejection is attainable by elevating pH above the pKa value, where borate ion is formed[11, 37]. The rejection of boron by RO is better for the borate ion due to its charge. Therefore adjusting pH is a key feature of removing boron by using RO. Bouguerra et al studied the amount of boron rejection vs. feed water pH was at different recovery rate (*Y*), their results are plotted in Figure 8[40].

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[3] Reserve osmosis

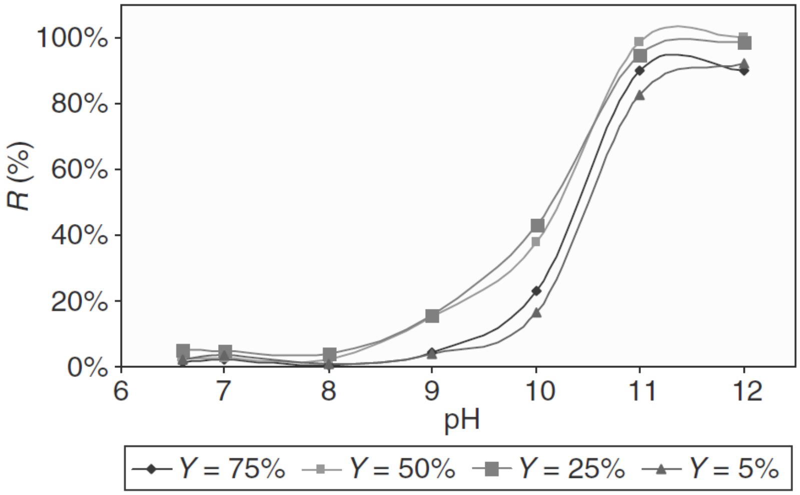

Figure 8. effect of pH on boron removal (Y indicates recovery rate)[40]

As a result single membrane or reserve osmosis procedure are not sufficient or cost effective for removing boron up to standard level and additional steps such as pH adjustment, utilizing ion exchange or multistage RO must be applied to achieve acceptable boron concentration.

Extensive review has been done by Tu et al in which they compare boron rejection efficiencies of some commercial membranes at standard test conditions. Results are shown in figure 9[44].

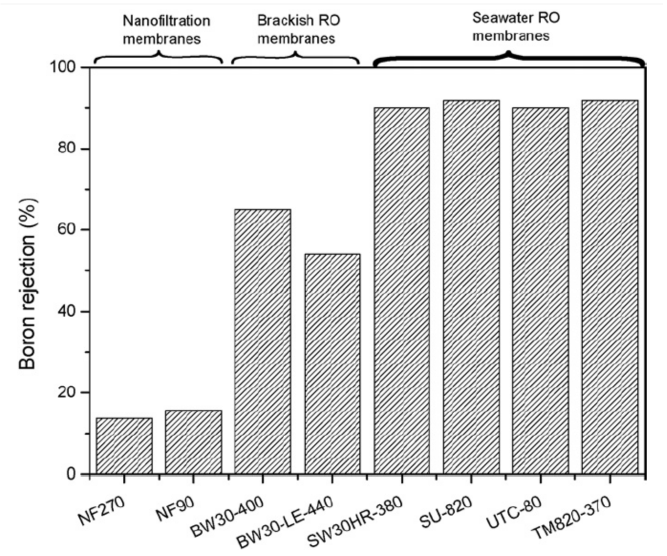

Figure 9. . Boron rejection efficiencies of some commercial membranes at standard test conditions

In another study, Cengeloglu et al investigated the removal of boron, using reverse osmosis (RO) technique and they compared three different membrane type: BW-30 (FILMTEC) and AG (GE Osmonics) and SWHR. They demonstrated that although, initial concentration of boron in solution affects boron concentration in permeate stream, it is not influential in rejection rate. Based on their experiment, the rejection of boron mainly depends on membrane type, pressure and pH of feed which is in agreement with pervious study. The maximum removal was observed by using SWHR membrane at pH of 11 at 30 bar pressure[45] .

4.5. Constructed wetland

As mentioned earlier, boron is present in domestic greywater due to everyday usage of detergents. Therefore the problem of removing boron from greywater becomes a concern due to its toxicity on plants and consequently it is necessary to reduce the boron level prior to any further application of treated greywater. The majority of removal processes, as discussed previously aimed to remove boron from industrial wastewater or seawater in large scale while constructed wetlands provide an opportunity of wastewater treatment for small community.

Aided by their complex biological and physical environments, constructed wetlands are able to detoxify wastewater by immobilizing and /or transforming contaminants to less toxic forms[46] . Based on most recent EPA design manual of constructed wetlands, they are categorized in two types: surface flow wetlands in which water flows above ground and through the leaves and stems of plants and subsurface flow wetlands in which level of water is below the ground and water flows through a media such as sand or gravel bed and roots of plants[47] . Figure 10 and 11 illustrate the schematic of each of those types.

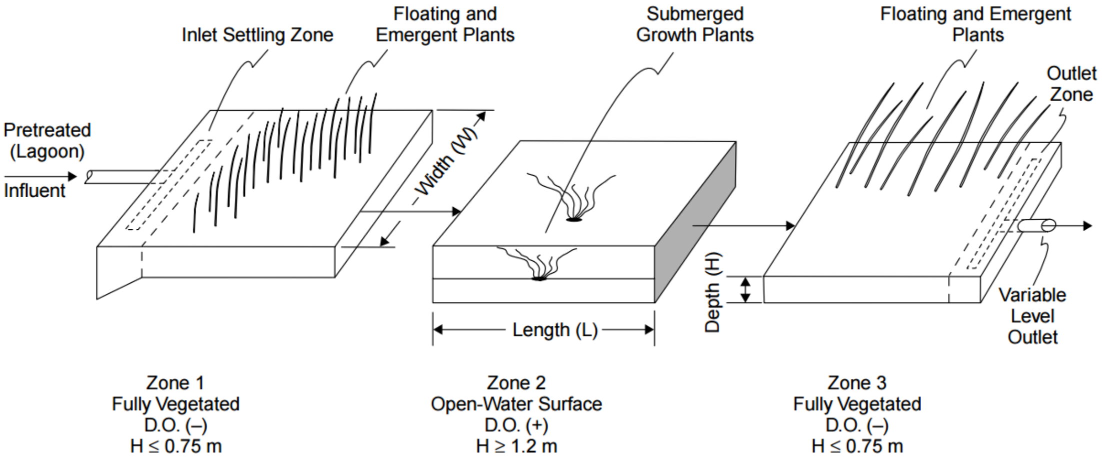

Figure 10. Elements of a free water surface (FWS) constructed wetland [47]

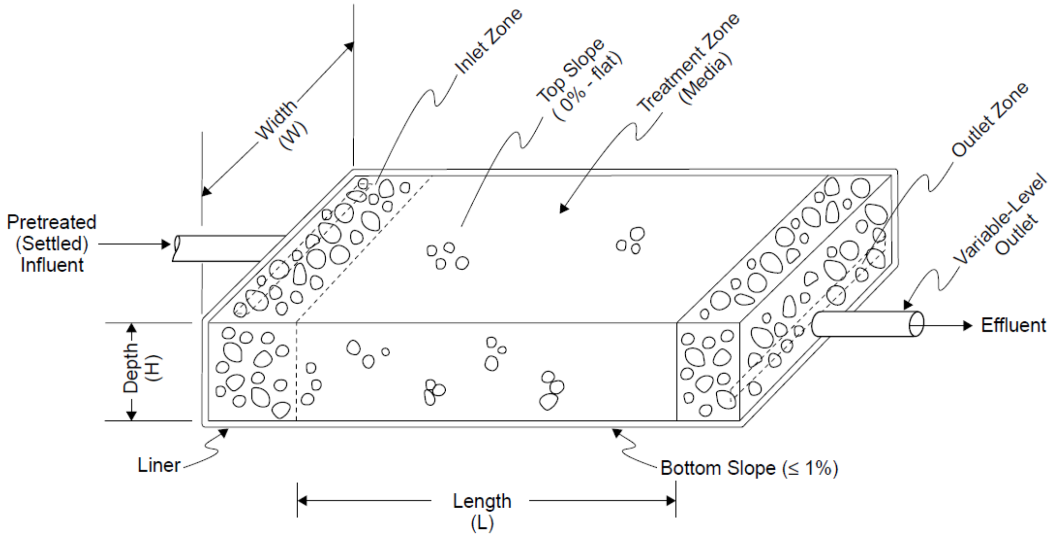

Figure 11. Elements of a vegetated submerged bed (VSB) system [47]

Figure 12 represents most common configuration of vertical flow constructed wetlands which is essentially a vegetated filter bed. The water flows vertically down through the filter matrix to the bottom of the basin where it is collected. Examining vertical flow wetland revealed that it is capable of removing organic load up to 90% as well as removing major nutrients such as nitrogen and phosphorous if an effective pretreatment procedure be applied[48].

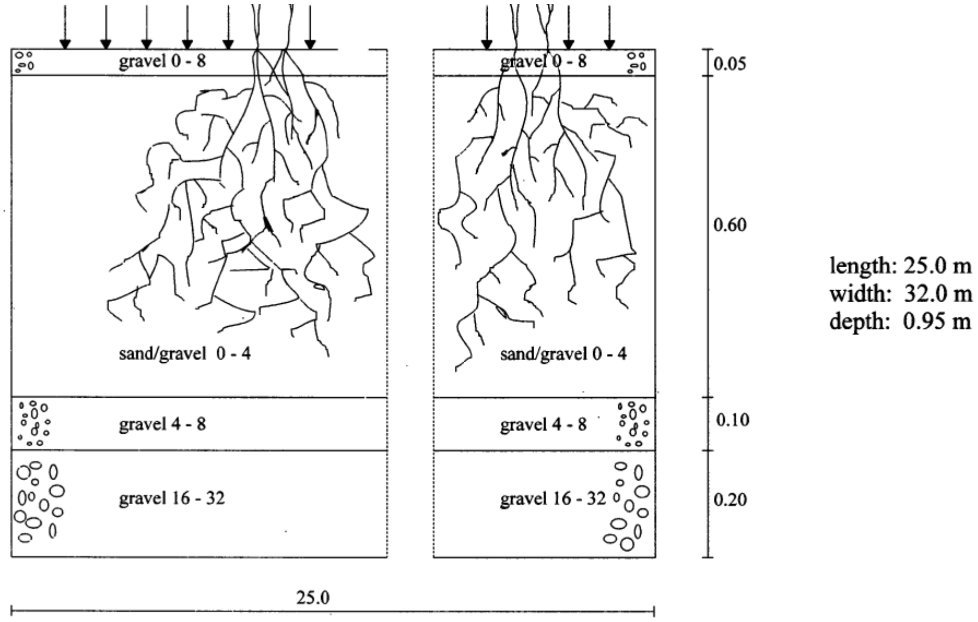

Figure 12. Cross sections of the constructed wetlands[48]

In an extensive wetland microcosm study, the ability fourteen common plants to wetland environment in the mid-western United States to accumulate selenocyanate, arsenic and boron from electric utility wastewater were tested. Microcosms were filled with coarse Colma and organic based potting medium and irrigated with nutrient solution for three months in order to promoting plant growth. It was calculated that residence time of water in each microcosm is about 12 days. Utility wastewater with boron concentration about 50 mg L-1 was introduced, after plant development. Figure 13 illustrates the concentration of boron inlet water (solid circles) and outlet water (solid triangles) of the treatment microcosms for next 42 days[46]. The wetland microcosms reduced the concentration of boron by 31%.

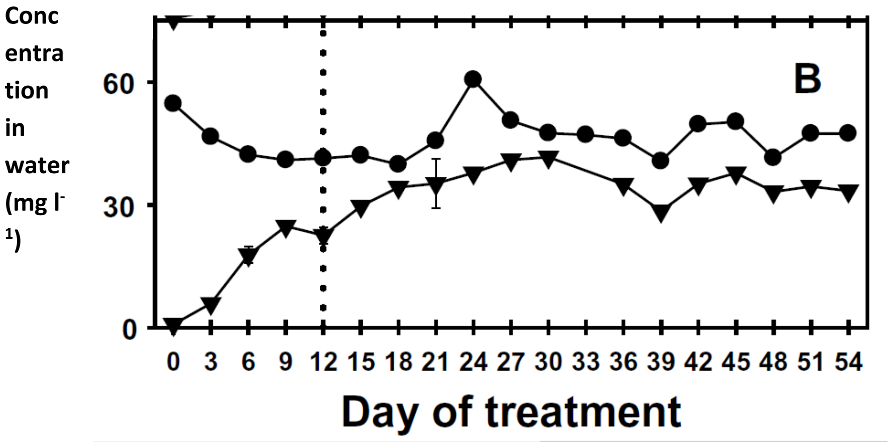

Figure 13. Concentration of boron in inlet and outlet water[46]

It was also demonstrated that not all plants have same capability in boron accumulation which is in agreement with previous studies. Experiment results determine that seven out of fourteen species survived and could accumulate boron in their structure; however they were only responsible for 3% of boron removal. Figure 14 represents the mass balance on boron removal. Based on this figure absorption to soil layer is the significant pathway for boron removal.

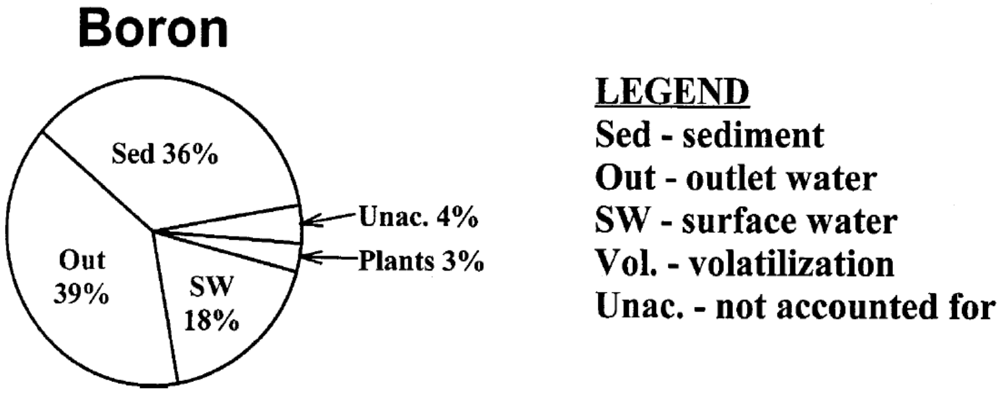

Figure 14. Mass balance of boron[46]

Another novel configuration that utilizes both tricking filter concept and constructed wetland is introduced by Gross et al. This system combines operational principles of trickling filter and vertical flow to treat greywater[2]. A trickling filter in general is a fixed-bed, biological reactor that operates under aerobic conditions. Continuous distribution of pre-settled wastewater over attached biofilm is a principal process considered for trickling filter. As the water migrates through the pores of the media, organics are aerobically degraded by the biofilm covering the filter material. Trickling filter can provide a simple, cost effective treatment for removing BOD in wastewater treatment[38].

Gross et al boosted previous method of vertical flow constructed wetland by collecting effluent and recycling it by the rate of 390 L h^{-1}. The pilot system was composed of two containers. The upper container consists of three layers of media which operate as infiltration, biological active or drainage layer. The lower container is designed for collecting water from upper one. The plants in this study were papyrus (*Cyperus haspan*) and pennyworth (*Hydrocotylr leucocephala*). About 65% of boron was removed from introduced greywater during short term study (Figure 15), however final concentration of 0.6 mg B L^{-1} in effluent was twice the amount of boron concentration in freshwater. Developed brown patches on lettuces which were irrigated with treated grey water indicate the elevated level of total boron. It was observed that boron mainly accumulated on soil layer rather than other layers or plants, therefore it was suggested that increasing soil volume or introducing more tolerant plants can increase boron removal from water [49].

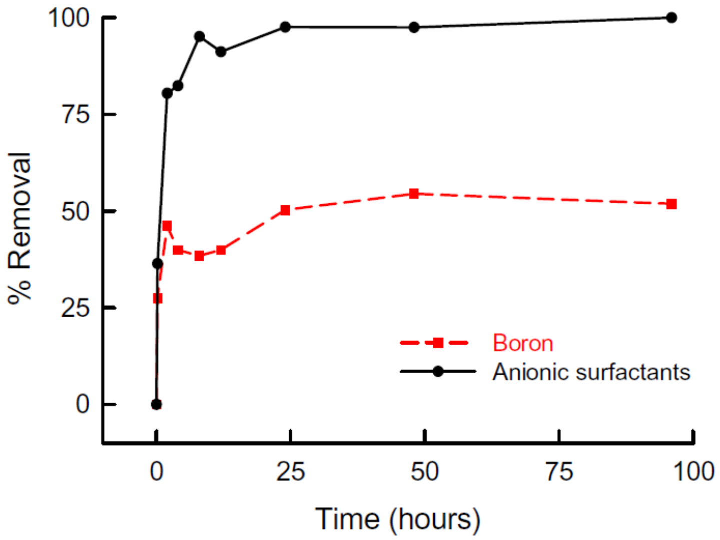

Figure 15. Percent removal of boron by a recycled vertical flow constructed wetland [49]

5. Discussion

5.1. Summary

In order to expand greywater application it is necessary to introduce safe, well treated greywater to environment. It is especially important to protect plants and animals from the toxicity that can be caused by high concentration of boron in greywater. Complex chemistry of boron and its dependence to pH impose a challenge on effective boron removal techniques. However, as discussed throughout the whole paper, boron can be removed from water and wastewater by various technologies. Comparative study reveals that each of those techniques has their own limitation and preferences. Although some techniques have a high potential for removing boron from water or wastewater, it should be noted that feasibility and practicality of those technologies are of a great concern for on-site greywater treatment. Table 11 summarizes advantages and disadvantages of previously reviewed techniques.

Table 11. Comparison of different boron removal technologies

Method	Advantages	Disadvantages
Chemical precipitation	Simple Well tested in laboratories	High pH or high temperature Voluminous amount of sludge Low concentration of boron
Adsorption	Less waste generation Moderate cost	Regenerating
Ion exchange	Utilize natural material Cost effective Durable	Competition between ions
Reverse osmosis	Continuous stream	Single reverse osmosis procedure is not sufficient Pretreatment requirement
Constructed wetland	Affordable Simple operation Reliability	10-65% removal Time consuming process Impact of climate change affect long term sustainability of wetland media

5.2. Recommendations

Based on extensive review on greywater applications and consequently boron removal techniques, following suggestions are proposed:

- Introducing of boron to greywater should be avoided or at least limited in the first place. This can be achieved by using more environmentally friendly detergents and soaps.
- On-site treatments that adopt constructed wetlands can examine plants that are more capable of boron accumulation.
- Landscape gardening can be modified by growing plants that are more tolerant toward boron.
- Natural ion exchange is a promising and affordable method that can be used in conjunction with other treatments (more experiments are needed).
- Potential of using different types of soil for boron adsorption should be investigated.

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