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## Boron in Produced Water: Challenges and Improvements: A Comprehensive Review

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**Abstract:** Boron concentration in produced water is significantly high. Produced water is water trapped in underground formation that is brought to surface along with oil and gas during drilling. Because this water has been in contact with the hydrocarbon formation for centuries, it now contains some of the characteristics of the formation as well as the hydrocarbons itself. Concisely, boron concentration in produced water makes produced water unusable if not properly removed. The World Health Organization (WHO) regulation guidelines for discharge of water into the environment set boron concentration at  $0.5 \text{ mg L}^{-1}$  for potable water. Many technologies have been developed to remove boron from produced water. However, there have been series of reported limitations based on the molecular weight of boron as well as its ionic dissociation constant. The health implication of boron consumption is enormous because according to the medico-biological investigations, boron compounds belong to the second class of the toxicological danger. The purpose of this study is to make an extensive review on published literatures on boron removal technologies in general, parameters that affect the efficiency of different treatment technologies, its importance, toxicity, deficiency and dissociation constant.

**Key words:** Adsorption, biological treatment, boron, electrocoagulation, electro dialysis, integrated system, ion exchange, parameters, reverse osmosis

### INTRODUCTION

Produced water includes water trapped in underground formations and water injected into the stratum to drive out the crude oil (Deng *et al.*, 2002). It is separated from crude oil above ground in an oil/water separator (Murray-Gulde *et al.*, 2003). In early stages of oil production, water content is usually low but can rise to as high as 80% during the later years of the well (Lu *et al.*, 2006). Produced water is the largest waste-stream of oil and gas exploration. Global produced water production is estimated at about 250 million barrels per day compared with about 80 million barrels per day of oil (Fakhru'l-Razia *et al.*, 2009). The chemical composition and behavior of produced water varies when compared with the surface waters because they are constrained within an aquifer (Wemedo *et al.*, 2009). Produced water has distinctive characteristics due to the presence of organic and inorganic matters, high salinity, BTEX, PAH, etc. which can cause toxicity to the environment. Naturally, produced water contains various microorganisms which result in microbial corrosion of the inner surfaces of pipes and related systems conveying the water. Such microbial corrosion process occurs by formation of biofilms on the metal surfaces (Puyate and Rim-Rukeh, 2008). The

constituents of produced water vary and can differ from well to well (Cakmakce *et al.*, 2008). The pH of produced water is about 6-8.5 (Cakmakce *et al.*, 2008; Veil *et al.*, 2004) while boron concentration in produced water is about 26-28 ppm (Cakmakce *et al.*, 2008). Produced water is increasingly being considered as a way to supplement limited freshwater resources in many parts of the US as well as other countries (Xu *et al.*, 2008). Therefore, effective treatment method should be employed to treat this essential water for reuse and irrigation purposes especially in arid areas where farmers experience water scarcity.

Boron is a commonly known drinking water contaminant that affects the reproductability of living organisms (Dydo *et al.*, 2005). In nature boron appears mostly as boric acid ( $\text{H}_3\text{BO}_3$ ) and borax, ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ). In aquatic systems, it exists primarily as undissociated boric acid and borate ions (Bryjak *et al.*, 2008). The main sources of boron in surface water are urban wastewater containing detergents and cleaning products, industrial effluents and chemical products used in agriculture (Liu *et al.*, 2009a). When water with high boron concentration is used for irrigation, boron compounds form complexes with heavy metals like Pb, Cu, Co, Ni, Cd etc. and increase the potential toxicity of these

**Table 1: Health hazard data of boric acid (Bryjak *et al.*, 2008)**

Acute health effects	Direct contact with solution may cause eye irritation. Boric acid may be absorbed through broken or abraded skin. Breathing mists may cause respiratory tract irritation
Inhalation exposure	Inhalation-breathing mist may cause irritation to the respiratory tract
Eye contact	May cause mild irritation upon prolonged exposure
Skin contact	Not irritating to skin. May be absorbed through injured skin and cause poisoning
Oral ingestion	May cause headaches; weakness and in coordination; nausea, vomiting, dizziness, diarrhea, drowsiness. May cause kidney damage
Chronic health effects	Reproduction/teratogenicity: A human study of occupationally exposed borate workers showed no adverse reproductive effects. Animal studies of inorganic borates showed reproductive effects in males. Mutagenicity: negative results of in vitro tests. Carcinogenicity: this substance has no evidence of carcinogenic properties. Health warnings: this product has low toxicity. Only large quantities may have adverse impact on human health. Target organs: kidneys

heavy metals. Serious health and environmental problems are caused when these complexes pass to groundwater (Sayiner *et al.*, 2008; Seki *et al.*, 2006; Seyhan *et al.*, 2007). Among all the elements of the periodic table, only carbon surpasses boron in variety of applications (Melnik *et al.*, 2005). The production of boron compounds has substantially increased recently due to increasing demand for these compounds in nuclear technology, rocket engines as fuels, production of heat resistant materials such as refractories and ceramics, high quality steel, heat-resistant polymers, catalysts, manufacture of glass, pharmaceuticals, corrosion inhibitors in anti-freeze formulations for motor vehicle and other cooling systems, dyestuff production, cosmetics, flame retardants, mild antiseptics, soaps, detergents, neutron absorber for nuclear installations, fertilizers, disinfectants, food preservatives etc. (Yilmaz *et al.*, 2008a; Cengeloglu *et al.*, 2007; Fujita *et al.*, 2005; Melnyk *et al.*, 2005; Yilmaz *et al.*, 2005; Magara *et al.*, 1998).

In soil, boron is available to plants as boric acid ( $H_3BO_3$ ), the form in which it is absorbed by root and transported. Boron plays an important role in plant carbohydrates metabolism, sugar translocation, hormonal action, functioning of the apical meristem, biological membrane structure and function, neutron capture therapy and other industrial products. Boron deficiency in plants may result in reduced growth, yield loss and even death of plant depending on the severity of the deficiency (Yilmaz *et al.*, 2008b). The range between deficiency and toxicity of boron is very narrow and influences the total uptake of anions in plants which also affect plant growth and development (Tariq and Mott, 2006). Boron is readily leached by rainfall and needs to be regularly replaced in a programme commensurate with irrigation, retentive properties of the soil and the requirements of the crops (Gupta, 1979). For humans, boron can represent reproductive dangers and has suspected teratogenic properties as shown in Table 1 (Bryjak *et al.*, 2008). Linder *et al.* (1990) and Redondo *et al.* (2003) reported that boron has presented impediments to male reproduction in studies carried out in laboratories. Studies in rats, mice and rabbits have demonstrated several developmental and teratogenic effects. In recent years, boron toxicity has gained an

**Table 2: Boron solubility in ( $g L^{-1}$ ) of cold water (Tariq and Mott, 2007)**

Common name	Formula	Solubility
Boric acid	$H_3BO_3$	51.5
Potassium tetraborate	$K_2B_4O_7 \cdot 5H_2O$	267.0
Sodium tetraborate (Borax)	$Na_2B_4O_7 \cdot 10H_2O$	16.0
Calcium metaborate	$Ca(BO_2)_2 \cdot 2H_2O$	3.1

**Table 3: Different plant tolerance for boron (Yilmaz *et al.*, 2008b)**

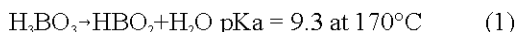
Sensitive $1 mg L^{-1}$ in irrigation water	Semi-sensitive $2 mg L^{-1}$ in irrigation water	Resistant $4 mg L^{-1}$ in irrigation water
Walnut	Sunflower	Asparagus
Plum	Potato	Palm
Pear	Cotton	Date-palm
Apple	Tomato	Sugar beet
Fig	Olive	Clover
Grape	Pea	Broad bean
Cheney	Barley	Bean
Peach	Wheat	Onion
Apricot	Corn	Turnip
Orange	Gruel	Cabbage
Grapefruit	Cruet	Lettuce
Lemon		Carrot

increasing interest because of the greater demand for desalinated water, in which boron concentration may be very high for healthy irrigation (Kaya *et al.*, 2009). Different authors have reported the role of salinity on toxicity of boron to plants. Yermiyahu *et al.* (2008) reported that salinity may reduce or increase boron toxic effect when both occur together while Ferreyra *et al.* (1997) reported that increased salinity decreases boron toxicity in numerous vegetables, rootstocks, wheat and chickpeas. Very low boron concentration is required in irrigation water for certain metabolic activities. However, if it is present in amounts higher than required, it becomes toxic (Fujita *et al.*, 2005; Ozturk and Kavak, 2008). Several factors affect boron availability to plants. Shaaban (2010) in his review, listed soil pH, soil texture, soil temperature/moisture, soil calcium carbonate and soil organic matter as factors affecting boron availability to plants. The solubility and retention of boron in soil depends on the various soil components and ions, specifically cations (K, Ca, Mg and Na) which readily combine with boron to form metaborates. Table 2 outlines the solubility of various boron compounds (Tariq and Mott, 2007). Therefore care is required in the management of this essential micronutrient in plants because the range between deficiency and toxicity is relatively narrow (Smith *et al.*, 2010). Plants tolerance to boron varies as outlined in Table 3.

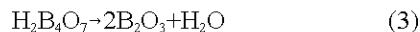
There is no easy method available for the removal of boron from water and wastewater (Bick and Oron, 2005; Liu *et al.*, 2009b; Melnyk *et al.*, 2005). Structural studies have indicated that in borates, the boron atom usually combines with either three or four oxygen atoms forming [BO<sub>3</sub>] or [BO<sub>4</sub>] groups. Accordingly, the electronic orbitals are hybridized to a planar SP<sup>2</sup> or a three-dimensional SP<sup>3</sup> structure (Xue *et al.*, 2000). The commonly used Reverse Osmosis (RO) desalination systems are not efficient enough in boron removal since boric acid might be transported through RO membranes in a manner similar to water (Kabay *et al.*, 2008a; Oo and Song, 2009; Turek *et al.*, 2007a). Conventional ion exchange is also inapplicable due to poor ionization of boron acid and requires periodical regeneration of resins when the ion exchange capacity becomes saturated (Melnyk *et al.*, 2005; Park *et al.*, 2007). Biological treatment is inefficient because of the complex boron chemistry. The objective of this review is to (a) Identify the factors affecting different treatment methods in removing boron from produced water (b) Examine the importance of integrated treatment process in removing boron from water (c) Suggest pre-treatment and post-treatment process for boron removal.

### CHEMISTRY OF BORON

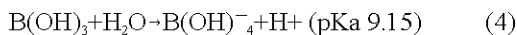
Boron is a metalloid and behaves as a Lewis acid (Arias *et al.*, 2011). The borate monovalent anion B(OH)<sub>4</sub><sup>-</sup> dominates at higher pH while non-ionized boric acid B(OH)<sub>3</sub> dominate at lower pH (Kabay *et al.*, 2010). The dissociation of boric acid in water can be described as follows:



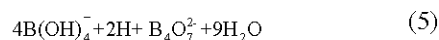
Further dissociation of boric acid in water occurs at higher temperature:



In aqueous solution, boric acid does not dissociate as a Bronsted acid but as a Lewis acid which interacts with water molecules to form tetrahydroxyborate ion (Arias *et al.*, 2011):



Between pH 7 and 10 and at high concentration (>0.025 mol L<sup>-1</sup>), polyborate anions are formed:



At lower pH, the dominant boron species is boric acid while at high pH, borate compounds predominate. This property of boron has been an obstacle to many treatment methodologies.

### TREATMENT TECHNOLOGIES

**Reverse Osmosis (RO):** Reverse osmosis is a major technology in wastewater treatment and have been used in removing different water contaminants. Newly produced seawater reverse osmosis membranes are claimed to have boron removal efficiency of 91-93% (Oo and Song, 2009). Conventional RO membranes reject boron to a level of about 40-78%. Single stage RO membranes are able to turn seawater of boron concentration (4-5 mg L<sup>-1</sup>) into permeate water with boron concentration of about 0.9-1.8 mg L<sup>-1</sup> (Sagiv and Semiat, 2004). This is because boric acid can diffuse through RO membrane in non-ionic form similar to that of carbonic acid or water. Rejection of boron by RO is better for the borate ion due to its charge while the rejection of non-ionized boric acid is low due to its smaller size and lack of electrical charge. Due to the absence of ionic charges at low pH, the hydration of the molecule results in a smaller size and less rejection of the molecule by a membrane. The dissociated form on the other hand will be fully hydrated, resulting in a larger radius and an enhancement of the negative charge of the ion. This results in higher rejection both by exclusion and repulsion by the negatively charged membrane (Redondo *et al.*, 2003). Because boric acid dominate at low pH, it is able to form bridges of hydrogen with the active groups of the membrane and diffuse in a similar way to that of carbonic acid or water (Fig. 1) (Pastor *et al.*, 2001). Several factors affect RO process. These factors include temperature, operating pressure and pH. Studies have shown that characterized parameters for selection of RO membranes should include zeta potential, contact angle, roughness and pore size distribution. Membrane surface roughness is also important in trapping of pollutants (Sarp *et al.*, 2008).

**Effect of pH:** Boron rejection depends greatly on pH (Magara *et al.*, 1998). With high salinity feeds such as seawater, boron rejection as high as 90% has been demonstrated but for low salinity waters, boron rejection very much depends on the pH level since pH determines the form of boron in water due to the equilibrium reaction between boric acid and borate ions (Bick and Oron, 2005). Higher pH levels result in appreciable decrease of boron

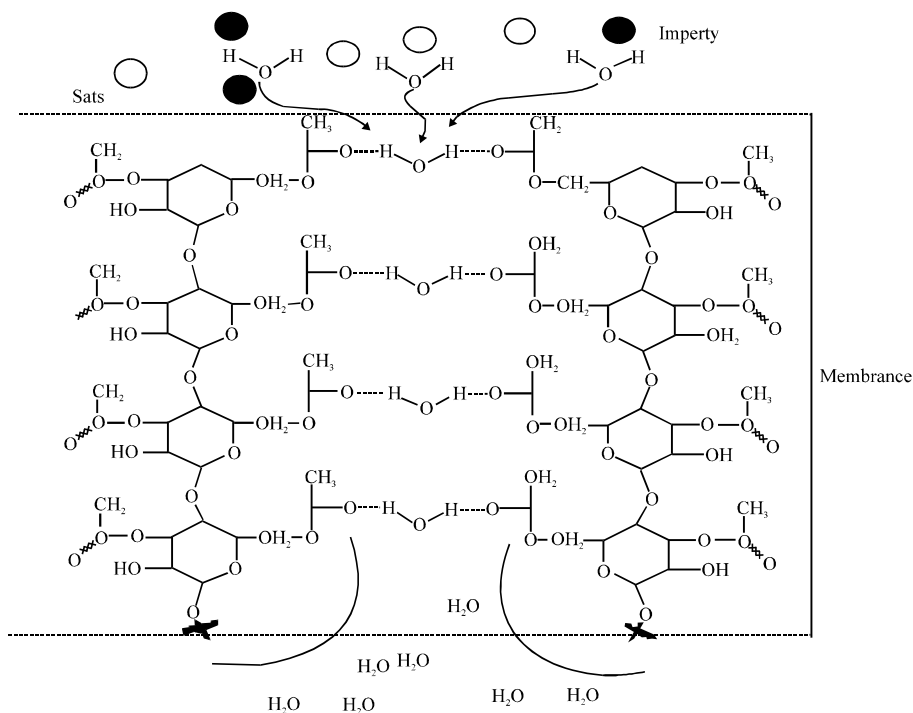


Fig. 1: Mechanism of H<sub>2</sub>O transport through reverse osmosis membrane by forming bridges of hydrogen (Pastor *et al.*, 2001)

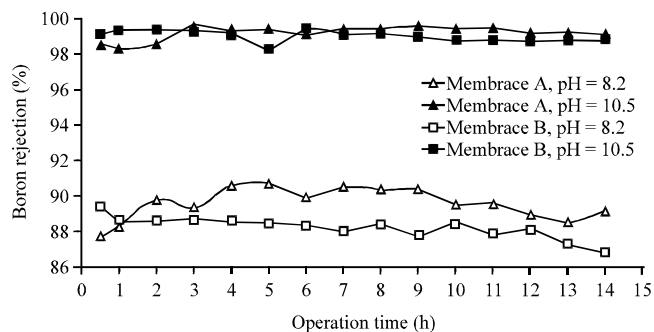


Fig. 2: Impact of solution pH on boron rejection by A and B membranes (batch concentration mode, pressure: 700 psi, Feed flow rate: 3.8 L min<sup>-1</sup>, Feed temp.: 22-24 EC) (Koseoglu *et al.*, 2008a)

in the permeate. This is because uncharged boron in the form of boric acid diffuses in the membrane for pH lower than 9.5. At high pH, boric acid transforms into borate ions (Bouguerra *et al.*, 2008). Potential precipitation of calcium carbonate and magnesium hydroxide at high pH in seawater reverse osmosis applications is a problem and must be avoided (Cengeloglu *et al.*, 2008). Koseoglu *et al.* (2008a) reported that a much higher boron rejection was obtained at pH of 10.5 (>98%) than those at natural seawater pH of 8.2 (about 85-90%) (Fig. 2). At high pH, there is stronger repulsion between membrane active surface and the charged borate ion which leads to the

enhanced boron rejection (Bonnelye *et al.*, 2007). Figure 3 shows dissociation of boric acid at various pH.

**Effect of operating pressure:** Increase in applied pressure increases the net pressure and consequently the permeate flux as well as rejection of particle across membrane (Binyam *et al.*, 2010). An increase in applied pressure results in an increase in water flux which leads to higher recoveries (Bonnelye *et al.*, 2007). Applied pressure also increases boron and salt rejections (Bouguerra *et al.*, 2008; Guler *et al.*, 2011). The higher the applied pressure, the higher the boron rejection (Magara *et al.*, 1998;

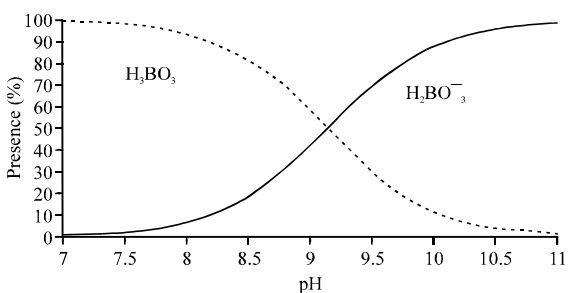


Fig. 3: Different forms of boron depending on pH, (Bonnelye *et al.*, 2007)

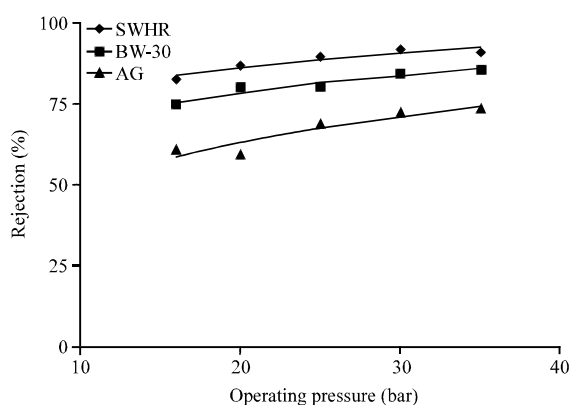


Fig. 4: Dependency of boron rejection on the operating pressure (Cengeloglu *et al.*, 2008)

Koseoglu *et al.*, 2008b). Figure 4 shows an upward trend in boron rejection as the applied pressure was simultaneously increased.

**Electrodialysis (ED):** Electrodialysis (ED) is a commonly used treatment technology. ED is an electrochemical process in which ions migrate through ion selective semi permeable membranes as a result of attraction to two electrically charged electrodes. It has high rejection for total dissolved solids, ions and colloids (Bick and Oron, 2005). Conventional ED is only capable of removing about 42-75% of boron (Yazicigil and Oztekin, 2006). Advantages of ED include high rejection of contaminants, low pressure requirement (lower than RO), requires minimal supervision in a remote setting, reject can meet effluent disposal limits and prevents scaling while its disadvantages include high capital and operating cost, high level of pre-treatment and frequent electrode replacement. Several factors affect the efficiency of boron removal by ED in produced water. They include interference of ions, pH of the sample and nature of the ED membrane. Studies have shown that chloride and sulfate affect boron transport in ED

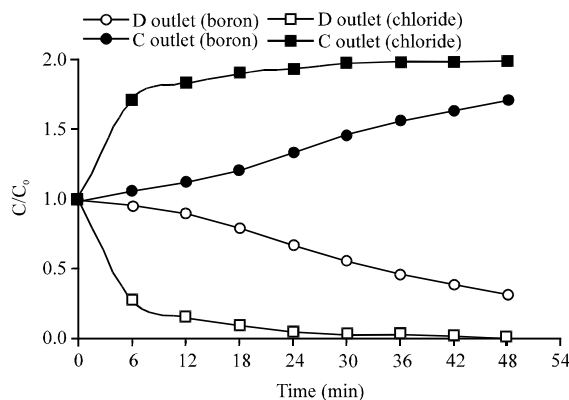


Fig. 5: Effect of chloride ions on boron removal (B:Cl equivalent ratio = 1:1; D: Dilute compartment, C: Concentrated compartment) (Kabay *et al.*, 2008b)

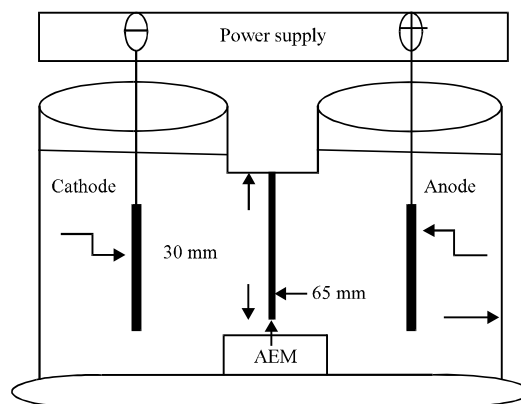


Fig. 6: A typical ED experimental diagram (Bandura-Zalska *et al.*, 2009)

(Bandura-Zalska *et al.*, 2009; Kabay *et al.*, 2008b). Salinity affects boron removal through electrodialysis. In a study of boron removal by electrodialysis, Kabay *et al.* (2008a) observed that chloride transported more quickly than borate ions (Fig. 5). Boron transport depends on ion charges and the hydrated radius of ions. Therefore, transport of boron becomes harder with increasing radius of ions and ion charges (Bandura-Zalska *et al.*, 2009). Increase in solution pH results in increase in transfer of boron. Also, increase in current density results in an increase in transfer of boron from the cathode chamber to the anode chamber. A typical ED diagram is represented in Fig. 6.

**Effect of interfering ions:** Transfer of boron by electrodialysis using anion exchange membranes is influenced by salinity. It is reported that in the presence of chloride, percent removal of boron decreases and

operation time increases while in the presence of sulfate, percent removal of boron did not change but operation time increased. This difference in transport property of boron in the presence of sulfate/chloride may be attributed to the hydrated radius of several anions present in the aqueous medium (Banasiak and Schafer, 2009; Turek *et al.*, 2007b). Bandura-Zalska *et al.* (2009) proposed an integrated process (desalination and ED) in boron removal because of the effect of interfering ions. Desalination is applied at low pH to remove ions at no boron transport while ED is applied at high pH to remove boron in the second stage since borate ions are present at high pH. The main goal of the preliminary stage is to reduce salinity at negligible boron transport as well as maximize desalination degree and rate at final concentrate boron level. Turek *et al.* (2007a) also used desalination and ED in removing boron from wastewater. It was observed that high initial dilute pH values do not enable reliable boron flux through the membrane. This may be due to high mobility and relative high content of hydroxide ions. The dissociation constant of  $B(OH)_3$  decreases with increasing NaCl concentration. NaCl concentration affects removal of other ions. Ions with smaller intrinsic crystal radii have higher hydration numbers, larger hydrated radii and hold their hydration shells more strongly. The larger the crystal ionic radius, the more diffuse the electric charge and the fewer water molecules surround the ion (Banasiak and Schafer, 2009). Kabay *et al.* (2008b) in their study, observed that more than 90% of chloride ions was removed from the solution in 18 min while only 20% of boron was removed along with chloride. After 42 min of operation time, almost all chloride ions were removed from the solution while about 40% of boron still exists in the solution (Fig. 7).

**Adsorption:** Adsorption is a process through which boron is adsorbed unto different kinds of particles. Many adsorbents have been used in adsorption process. They include cerium oxide (Ozturk and Kavak, 2008), activated carbon prepared from coconut shell impregnated with calcium and barium chlorides, citric and tartaric acids (Rajakovic and Ristic, 1996), activated alumina (Bouguerra *et al.*, 2008),  $Al_2O_3$  based materials (siral 30 and pural) (Seki *et al.*, 2006), activated carbon impregnated with salicylic acid (Celik *et al.*, 2008), iron-rich natural clays (Seyhan *et al.*, 2007), activated sludge (Fujita *et al.*, 2005), neutralized red mud (Cengeloglu *et al.*, 2007) and composite magnetic particles (Liu *et al.*, 2009b). Several factors affect adsorption of boron. They include loss of adsorbent, geometry of the system, the flow of water solution through the pores of the system, the diffusion rate, adsorbent dose and the kinetics of the surface reactions (Ozturk and Kavak, 2008).

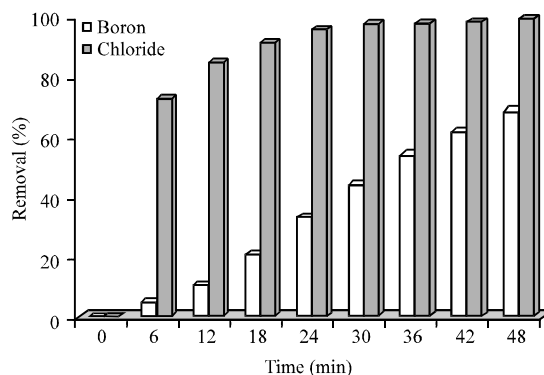


Fig. 7: Separation of boron in the presence of chloride ions (B:Cl : 1:1 (Kabay *et al.*, 2008b)

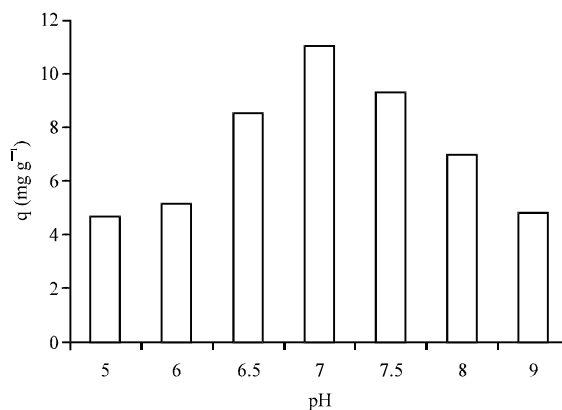


Fig. 8: Effect of pH on the adsorption of boron on cotton cellulose ( $C_0 = 500 \text{ mg L}^{-1}$ ,  $m = 0.1 \text{ g}$ ,  $V = 50 \text{ mL}$ ) (Liu *et al.*, 2007)

Sample pH is a determinant of boron removal in adsorption study (Garcia-Soto and Camacho, 2006). Depending upon the nature of adsorbents, Irawan *et al.* (2011) reported that borate concentration in the solution and its adsorption are both pH-dependent and the optimum pH of boron adsorption is 2 for fly ash, 6.0 for composite magnetic particles, 7 for neutralized red mud and 9 for layered double hydroxide. Solution pH affects both boron speciation and surface properties of sorbent (Wei *et al.*, 2011). The amount of removed boron increases with increasing adsorbent dose due to the increase in the total available surface area of the adsorbent particles (Yazicigil and Oztekin, 2006). Studies have shown that different adsorbents have varying adsorption capacities (Bouguerra *et al.*, 2008; Ozturk and Kavak, 2008; Seki *et al.*, 2006; Yilmaz *et al.*, 2005). Figure 8 represents the effect of pH on boron adsorption on cotton cellulose. Different adsorbents have different adsorption capacities. Table 4 is a compilation of different adsorbent materials with their adsorption capacities.

**Effect of adsorbent dose:** It is essential to determine the amount of adsorbent that is required for an experiment (Garcia-Soto and Camacho, 2006). Increase in adsorbent dose increases the surface area of the adsorbent particles. Boron removal increased with increase in red mud dosage as a result of the increase in total available surface area of the adsorbent particles. Therefore, the higher the adsorbent concentration, the lower the boron level in the permeate (Bryjak *et al.*, 2008). Figure 9 represents variation of boron removal with red mud dose (Cengeloglu *et al.*, 2007).

Table 4: Different adsorbents and their adsorption capacities

Adsorbent	K (mg g <sup>-1</sup> )	N
Activated carbon	0.190	2.5
Activated alumina	0.440	1.4
Minespoils (Woolley Edge)	0.004	1.4
Minespoils (Hoyland Common)	0.005	1.6
Minespoils (Crowedge)	0.002	1.9
Neutralized red mud	5.996	2.2

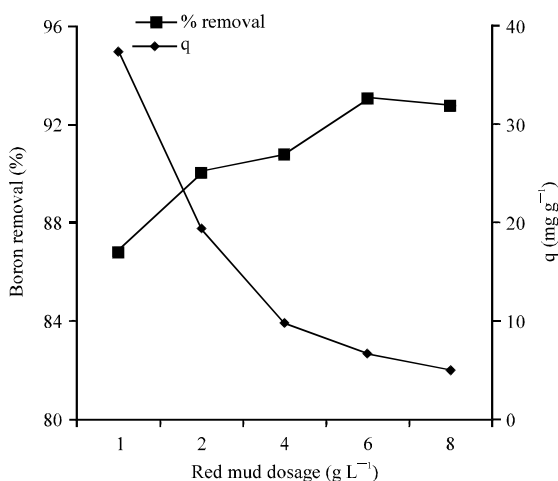


Fig. 9: Variation of boron removal with red mud dose. Initial boron concentration: 43 mg L<sup>-1</sup>, pH 7, agitation speed: 500 rpm and temperature: 25±1 °C. (Cengeloglu *et al.*, 2007)

**Ion exchange:** Ion exchange is one treatment process that has gained wider application in boron treatment. The use of selective ion exchange resins (Purolite and Diaion) have not only been efficient in removing boron from wastewater but also in recovering boron from wastewater (Kabay *et al.*, 2004). The most commonly used resins are the Amberlite IRA-743, otherwise known as Amberlite XE-243 and Diaion CRB 02 and Dowex XUS 43594.00 (Kabay *et al.*, 2008c). These resins are macroporous polystyrene based resin, with functional groups specially designed for the selective removal of salts of boron from aqueous solutions. They are effective for solutions over a wide range of pH values and over a wide range of boron concentrations. These boron selective resins show great elimination performance and the sorption kinetics of both resins fit well to pseudo-second-order kinetics model (Shpiner *et al.*, 2009). This complex formation is not pure ion exchange and therefore does not require ionization of boric acid. The resin performance is not affected by temperature variations, by pH value or by the background salinity of the water to be treated. Selective sorption of boron by these sorbents is as a result of formation of stable complexes like ethers or complex anions with polyoxicomounds. These resins used in ion exchange system have a macroporous polystyrene backbone and a very specific functional group based on N-methyl glucamine which has a tertiary amine end and a polyol end and makes a very stable complex with boric acid (Jacob, 2007). Boron removal efficiency here is reported to be about 93-98% (Melnyk *et al.*, 2005). A typical ion exchange selective resin is shown in Fig. 10.

Uptake of boron by this selective ion exchange resin is high. An evaluation study with Diaion (CRB 02) and Dowex(XUS 43594.00)resins by Kabay *et al.* (2006) shows that both resins have almost similar boron adsorption capacity and are efficient in removing boron from solution

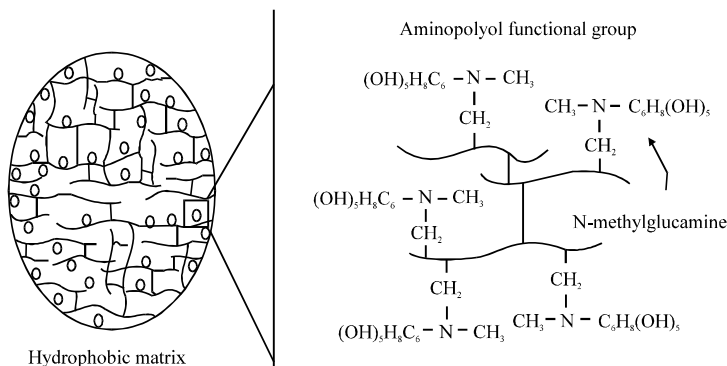


Fig. 10: Chemical structure of boron selective resin containing N-methyl glucamine (Kabay *et al.*, 2008c)



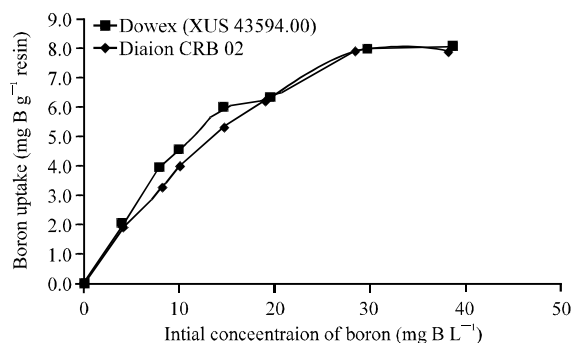


Fig. 11: Boron adsorption isotherms of Diaion CRB 02 and Dowex (XUS 43594.00) resins (Kabay *et al.*, 2006)

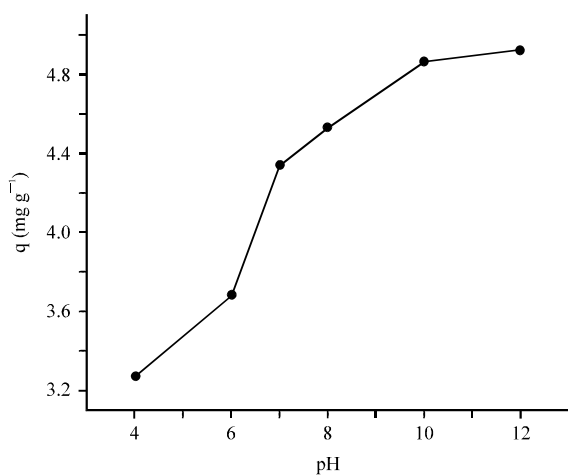


Fig. 12: Effect of pH on boron removal (Yan *et al.*, 2008)

as shown in Fig. 11. The advantages of these selective ion exchange resins over the conventional ion exchange treatment are that they are not affected much by pH of solution or concentration.

The mobility and hydrated radius of ions affects boron transport in an ion exchange process (Kir *et al.*, 2011). An increase in pH increases removal of boron by the resin since the resin can only extract the ionic form of boron (Fig. 12). An increase in temperature also increases the removal of boron from brine (Yan *et al.*, 2008).

**Biological treatment:** Biological treatment of produced water is still in its infancy (Shpiner *et al.*, 2009). Reported literatures on boron removal through biological treatment are scarce. Previous works have been mainly laboratory/pilot scale experiments of aerobic and anaerobic treatment such as activated sludge (Tizghadam *et al.*, 2008; Dincer, 2004; Tellez *et al.*, 2002), aerated lagoons (Boiran *et al.*, 1996; Montalvo *et al.*, 2010), SBR system (Li *et al.*, 2003; Xiao *et al.*, 2008), immobilized cells system (Li *et al.*, 2005; Lu *et al.*, 2009;

Wang *et al.*, 2008), Biodegradation (Rezaee *et al.*, 2006), dinitrogen fixation (Perona *et al.*, 1991), sulfate removal (Chen *et al.*, 2009; Zhou *et al.*, 2011; Zhao *et al.*, 2009), activated sludge, sand filters and activated carbon (Al-Jlil, 2009), sulfidogenic bacteria (Agrawal *et al.*, 2010; Kaura *et al.*, 2009), geochemical influence and biokinetics (Orphan *et al.*, 2004; Tellez *et al.*, 1995), Semi-continuous and continuous anaerobic treatment (Hong *et al.*, 2009).

Various biomass species have been used in a single and combined process to treat produced water but there have been marked inefficiencies from literature over their ability to feed on colloids. Single step biological treatment has proved ineffective in removing many pollutants of wastewater. Conventional biological treatments have not been effective enough to reduce boron to its standard limit level for irrigation (Linares-Hernandez *et al.*, 2010). One of the biological treatment methods that have been used in the treatment of wastewater pollutants is Waste Stabilization Ponds (WSPs). WSPs incorporate the activity of phototrophic, autotrophic and heterotrophic microorganisms, requires little or no energy and play important role in the removal of pollutants. Oxidation ponds are characterized by a high surface area and retention times of a few days to a few weeks. The biodiversity in the ponds may also influence the potential of the process to degrade a wide range of petroleum-derived compounds including the full or partial degradation of slowly degradable and recalcitrant material. WSPs have a large volume which enables them to tolerate shock loads and efficiently remove heavy metals (Shpiner *et al.*, 2009). In a study of biological treatment of boron containing wastewater by activated sludge conducted by Dincer, 2004, it was observed that boron concentration affected COD removal rate when compared with the COD removal rate of a boron free wastewater. Whereas the COD concentration of a boron free wastewater in the reactor reached a steady state level of 20 mg L<sup>-1</sup> after 9 h of operation, resulting in a COD removal rate of 75.39 mg L<sup>-1</sup> h<sup>-1</sup> and a removal efficiency of 98% at a loading rate of 76.92 mg L<sup>-1</sup> h<sup>-1</sup>, the COD removal rate of a boron containing wastewater for feed boron levels lower than 2500 mg L<sup>-1</sup> has efficiencies of about 80%. However, when the feed boron level is higher than 2500 mg L<sup>-1</sup>, the system did not reach steady state and the COD removal rate decreased. The rate of COD removal also decreased with increasing boron in the feed wastewater, as shown in Fig. 13. The COD removal rate was nearly 75.39 mg L<sup>-1</sup> h<sup>-1</sup> with boron free wastewater and decreased to a value of 45.39 mg L<sup>-1</sup> h<sup>-1</sup> for 5000 mg L<sup>-1</sup> boron concentration, indicating approximately 40% reduction.

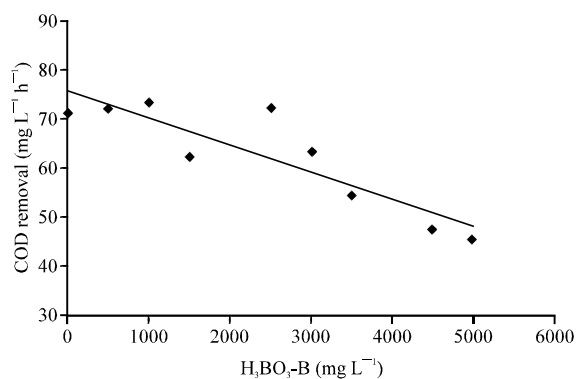


Fig. 13: Variations of total COD removal rate with H<sub>3</sub>BO<sub>3</sub>-B concentration in feed wastewater at steady-state (Dincer, 2004)

**Electrocoagulation (EC):** Electrocoagulation (EC) is the process of destabilizing suspended, emulsified or dissolved contaminants in an aqueous medium by introducing an electric current into the medium (Emamjomeh and Sivakumar, 2009). EC is based on the valid scientific principle of water response to strong electric field. EC is an emerging treatment technology which has been applied with success in wastewater treatment (Linares-Hernandez *et al.*, 2010). Electrocoagulation involves the generation of coagulants in situ by electrical dissolution of the sacrificial anode and involves the following three mechanisms; electrode oxidation, gas bubble generation, flotation and sedimentation of flocs formed (Emamjomeh and Sivakumar, 2009).

EC presents similar advantages as chemical coagulation and reduces its disadvantages which results in higher yields and less waste sludge (Essadki *et al.*, 2009). The advantages of EC include high particulate removal efficiency, compact treatment facility, relatively low cost and possibility of complete automation (Aoudj *et al.*, 2010; Chen, 2004). EC is characterized by a fast rate of pollutant removal, simplicity in operation and low capital and operating costs (Chen *et al.*, 2000). EC has been used in reducing boron to the World Health Organization (WHO) standard limit of 0.5 mg L<sup>-1</sup>. The efficiency of EC depends on sample pH, current density, temperature, boron concentration, electrode spacing and treatment time. pH is an important parameter influencing the performance of the electrochemical process because pH determines the ionic form of boron (borate ions) (Balasubramanian *et al.*, 2009). At higher inter-electrode distance, rate of aggregation of suspended particles as well as adsorption of contaminants will be low. At minimum inter electrode distance, the resistance for current flow in the solution medium is lower and that

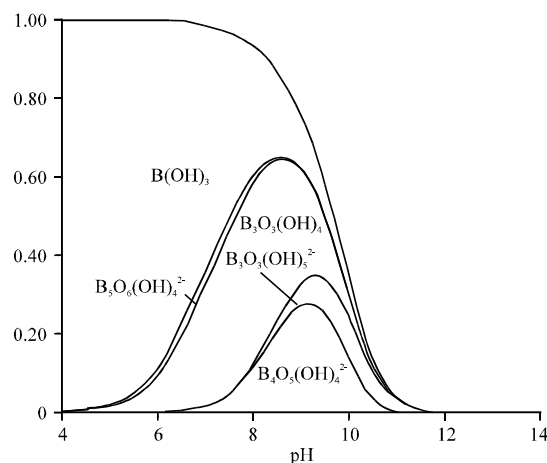


Fig. 14: Changing of borate ions species depending on pH

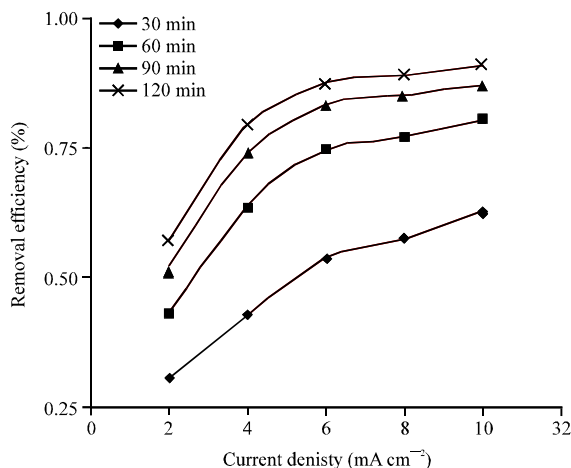


Fig. 15: Effect of current density on boron removal pH in aqueous media (Yilmaz *et al.*, 2007) (Yilmaz *et al.*, 2008a)

facilitates the electrolytic process for enhanced removal (Ghosh *et al.*, 2008). The current density is the current per unit surface; it is a parameter that controls the anode dissolution speed on the one hand and that of hydrogen formation on the other hand (Nanseu-Njiki *et al.*, 2009). Effect of pH and current density on EC is represented in Fig. 14 and 15.

Boron removal efficiency of 95% with electrocoagulation was reported by Yilmaz *et al.* (2008b) (Fig. 16). Electrocoagulation can be an efficient means of removing boron from wastewater in a cost effective way when the operating parameters are favorably combined.

**Integrated system:** Different treatment techniques can be combined to treat produced water. Some studies have used integrated process to treat produced water.

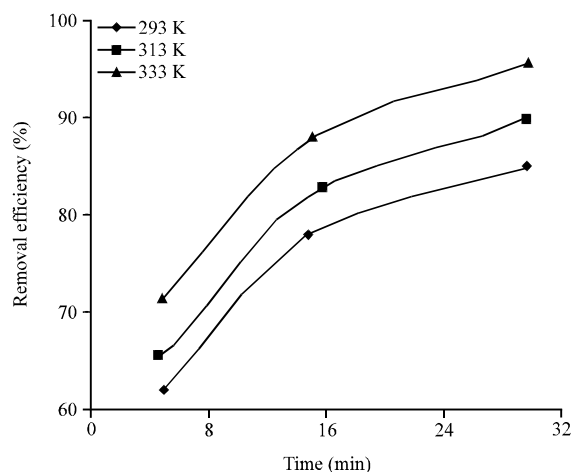


Fig. 16: The effect of temperature on boron removal ( $3.0 \text{ mA m}^{-2}$  current density, pH 8.0 and 150 rpm stirring speed) (Yilmaz *et al.*, 2008b)

Ebrahimi *et al.* (2010) used Microfiltration (MF) and Ultrafiltration (UF) as a pretreatment step and Nanofiltration (NF) as the final step in the treatment of oilfield produced water. Turek *et al.* (2005) studied adsorption/co-precipitation process coupled with reverse osmosis. Li *et al.* (2010) investigated the effects of the combination of anaerobic process and micro-electrolysis in the removal of COD and biodegradables. The integrated system can be used to remove boron from produced water. Each component of the integrated system should be operated at its best operating condition. However, the cost of such combination should also be taken into consideration to ascertain its feasibility. Various membrane methods like MF, UF, NF and RO can be combined, RO and ED; Micro-electrolysis and biological treatment; EC and biological treatment/RO; adsorption/co-precipitation/RO; ion exchange and RO, 2 pass RO with increased pH especially in the 2nd pass etc.

### CONCLUSIONS

Boron is a complex compound and its behavior in water has made its removal very difficult. One of the best ways to reduce boron problem is to reduce the level of its pollution anthropogenically. Therefore, perborates used in detergent products should be regulated because it also increases the quantity of boron in surface water. The treatment technologies enumerated in this study have shown their ample abilities in removing boron from wastewater but their efficiencies depend on the operating conditions of each system. Reverse osmosis should be equipped to remove boron at one stage pass. This can be achieved by manufacturing membranes that will enable

more investigation on boron removal based on transport equation and not in terms of flux and salt rejection only. Pre-treatment or post-treatment of wastewater through an integrated process results in effective treatment. However, these integrated systems should be arranged in such a way that the systems will be compatible to each other and also operate at their optimal efficiencies. In the case of boron, produced water should be pre-treated to recover boron based on its wide importance and applicability.

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