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Review Article

A Review on Boron Pollution and Its Removal Techniques

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ABSTRACT

Boron is one of the minor elements dissolved in natural water and one of the seven essential micronutrient elements required for the normal growth of most plants. Boron is a commonly known drinking water contaminant that affects the reproductability of living organisms. In nature boron appears mostly as boric acid (H_3BO_3) and borax, ($Na_2B_4O_7.10H_2O$). In aquatic systems, it exists primarily as undissociated boric acid and borate ions. The main sources of boron in surface water are urban wastewater containing detergents and cleaning products, industrial effluents and chemical products used in agriculture. 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 heavy metals. In recent years, boron toxicity has gained an increasing interest because of the greater demand for desalinated water, in which boron concentration may be very high for healthy irrigation. There is no easy method available for the removal of boron from water and wastewater. Structural studies have indicated that in borates, the boron atom usually combines with either three or four oxygen atoms forming [BO_3] or [BO_4] groups. Accordingly, the electronic orbitals are hybridized to a planar SPor a three-dimensional SP^3 structure. 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. 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. Biological treatment is inefficient because of the complex boron chemistry. An extensive survey of the literature has been conducted related to technologies that have been developed for boron removal from wastewater. Only the publications concerned with the removal of boron from aqueous solutions have been reviewed and summarized in this paper.

Keywords: Boric acid, Borax, Biological treatment, Reverse osmosis.

INTRODUCTION

The quality of our environment is deteriorating day by day with the largest cities reaching saturation points and unable to cope with the increasing pressure on their infrastructure. Industrial effluents, sewage and farm wastes are the major pollutants contaminating the environment. The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury, arsenic, boron and thallium. These metals have been extensively studied (except boron and thallium) and their effects on human health regularly reviewed by international bodies such as the WHO. World Health Organization (WHO) and European Union (EU) have set up a limitation of boron level of 0.5 mg L^{-1} in potable water.

Boron is a commonly known drinking water contaminant that affects the reproductability of living organisms **[1].** In aquatic systems, it exists primarily as undissociated boric acid and borate ions [2]. The main sources of boron in surface water are urban wastewater containing detergents and cleaning products, industrial effluents and chemical products used in agriculture **[3]**. 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 heavy metals.

Serious health and environmental problems are caused when these complexes pass to groundwater [4]. Among all the elements of the periodic table, only carbon surpasses boron in variety of applications [5]. 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 [6].

Boron is also an essential element for plants, animals and human beings. For plants, boron plays a role in carbohydrate metabolism, sugar translocation, hormone action, normal growth and functioning of the apical meristem, nucleic acid synthesis, and biological membrane structure and function [7]. Boron deficiency can cause a series of damage to plants, such as retardation of root and leaf growth, bark splitting, retardation of enzyme reactions and leaf photosynthesis, and even can lead to a death of plants. For animals and human beings, boron relates to immune function of organisms, it also has effects on bone metabolism and central nervous system function. Lack of boron may lead to malformations of embryos grown for vertebrates and cause low absorption efficiency for nutrient elements such as Calcium, Magnesium and phosphorus [8].

In recent years, boron toxicity has gained an increasing interest because of the greater demand for desalinated water, in which boron concentration may be very high for healthy irrigation [9]. Different authors have reported the role of salinity on toxicity of boron to plants. Yermiyahu *et al.* [10] reported that salinity may reduce or increase boron toxic effect when both occur together while Ferreyra *et al* [11] 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 [12]. 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. Therefore, care is required in the management of this essential micronutrient in plants because the range between deficiency and toxicity is relatively narrow [13].

There is no easy method available for the removal of boron from water and waste water [14]. 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 [15]. 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 [16]. Biological treatment is inefficient because of the complex boron chemistry. The objective of this research work is to suggest pre-treatment and post-treatment process for boron removal by using prepared activated carbons.

Chemistry of Boron [17]**:** Boron is a metalloid and behaves as a Lewis acid [18]. The borate monovalent anion $B(OH)_4^-$ dominates at higher pH while non-ionized boric acid $B(OH)_3$ dominate at lower pH. The dissociation of boric acid in water can be described as follows:

$$H_3BO_3 - HBO_2 + H_2O \ pKa = 9.3 \text{ at } 170°C$$

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

$$4HBO_2 - H_2B_4O_7 + H_2O \ (300°C)$$
$$H_2B_4O_7 - 2B_2O_3 + H_2O$$

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:

$$B(OH)_3 + H_2O - B(OH)^-_4 + H+ \ (pKa\ 9.15)$$

Between pH 7 and 10 and at high concentration (>0.025 $molL^{-1}$), polyborate anions are formed:

$$4B(OH)_4^- + 2H + B_4O_7^{2-} + 9H_2O$$

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.

Removal Methods: In the past few decades, numerous of separation technologies have been applied in the boron removal from aqueous solutions, including adsorption, reverse osmosis (RO), ion exchange, electrocoagulation, Donnean dialysis, chemical coagulation, hybrid process etc.,

Conventional methods for boron removal include ion exchange, reverse osmosis, and adsorption/precipitation. A drawback of ion exchange and RO is that the boron concentrates in a regenerate solution or RO concentrate which are difficult to treat and dispose of. Adsorption/precipitation methods offer the advantage that boron waste is incorporated into a solid, which might be disposed of more easily.

Patricia Remy *et al* [19] studied removal of boron from Wastewater by precipitation of a sparingly soluble salt. Experimental results show that under optimal conditions (50 g L^{-1}) of powdered calcium hydroxide, a temperature of 90°C, and process time of 2 h), the residual boron concentration in solution was reduced from 700 to less than 50 mg L^{-1} a value never reached before by a precipitation process.

Okay *et al* [20] investigated various methods and evaluated two effective processes for removing boron from wastewater, based on adsorption on magnesium oxide and ion exchange. Unfortunately, the large consumption of chemicals and expensive regeneration steps for boronspecific resin make these technologies uneconomical.

Yu-Jen Shih *et al* [21] studied Treatment of high boron concentration wastewater by chemical oxo-precipitation (COP) at room temperature. Chemical oxo-precipitation (COP) process that combined the oxidant treatment and precipitation using metal salts was developed for boron containing water disposal under relatively milder conditions (room temperature, pH 10) than a precipitation process. The residue boron in end water of COP was 15 mg L^{-1}, a value never reached by the conventional coagulation processes.

Boron removal was studied by Mebrure Badruk *et al* [22] using N-glutamine-type resins Dianion CRB 02 and Puro lite S 108. The resin Dianion CRB 02 exhibited a higher sorption capacity for boron removal from 0.01 M H_3BO_3 solution than did Purolite S 108. The presence of calcium, sodium, and chloride ions did not make a large interference on boron removal by both Dianion CRB 02 and Purolite S 108 resins.

Boron adsorption and co-precipitation to a variety of amorphous or crystalline minerals has been demonstrated [23]. Many of these processes have been used as portions of existing water treatment facilities. For example, Turek, *et al* [24] used iron, nickel and aluminum hydroxides on landfill leachate RO concentrate to remove boron to levels less than 1 mg L^{-1}.

A further study on boron removal by adsorption on magnesium oxide was conducted by Garcia-Soto and Camacho [25]. They carried out their study on two solutions, one with a high concentration (500 mg B L^{-1}) and one with low concentration (50 g L^{-1}). The removal yield was quantified by the mg/B ratio so that the amount of additional boron removal achieved per additional amount of magnesium oxide added could be quantified. Removal yield correlated with mg/B ratio up to a ratio of 20.

Yilmaz *et al* [26 compared electrocoagulation and chemical coagulation for boron removal. Specifically, aluminum chloride addition was compared with aluminum electrocoagulation. Aluminum doses were equal for both methods (7.45 g L^{-1}). Optimal pH was found to be the same for both coagulation methods at a pH of 8.0. It was also found that removal saturated for both methods above 100 mg L^{-1} initial concentration.

EishiYoshikawa *et al* [27] developed a method to Removal of boron from wastewater by the hydroxyapatite formation reaction using acceleration effect of ammonia. The removal rate of boron was controlled by the HAp precipitate formation. This method could reduce reaction time to 1/10 that of the conventional one. The addition of ammonia could accelerate boron removal in this proposed method. Sodium alpha-olefin sulfonate was the most effective coagulant in proposed method. The proposed method had applicability to the real waste water sample.

Activated carbon (AC) has a strong adsorption capacity because of its high specific surface area, which is the most widely used sorbent in industrial and environmental applications. However, there are few researches using AC for boron removal, the main reason is that AC has less surface-active group of boron, which caused low adsorption selectivity.

Köse *et al* [28] investigated the removal capacity and the conditions that control boron retention using AC, which prepared from olive bagasses by physical activation. The maximum boron removal capacity was 3.5 mg g^{-1} obtained at initial pH 5.5, and the experiment indicated that the adsorption kinetics fit both the pseudo-fist-order model and intraparticle diffusion model well.

Can *et al* [29] developed salicylic acid impregnated AC to remove boron from aqueous. The adsorption experiment reached equilibrium within 10 min, and the experimental data followed the pseudo second-order kinetic model very well. Besides, the experimental result was suitable for Langmuir isotherm.

Halim *et al* [30] investigated the boron adsorption properties on curcumin-impregnated AC. The maximum boron load capacity was 5.0 mg/g according to the Langmuir model, which was much higher than bare AC. And curcumin-impregnated-AC can be reused with slightly lower adsorption capacity.

Kluczka *et al* [31] used several impregnated ACs to adsorb boron from aqueous. In the static system, the best sorbent was AC impregnated with tartaric acid. While in the dynamic system, AC impregnated with mannitol got the maximum boron adsorption ability.

A number of researches using natural materials have been carried out too. According to different material characteristics, natural material sorbents can be divided into two major parts. One is natural minerals like saprolite, red mud, cristobalite, alunite, etc. The other is plant materials, such as seeds of plants, natural polymers. Extensive source and lower price are main advantages of natural material sorbents, which is confirmed to be the requirement of low- cost boron removal processes for water treatment [32].

CONCLUSION

This review presented several sorbents for boron removal from aqueous solutions. And the general trends of the current study of the boron sorbents can be concluded given cost issue for boron removal, many low-cost sorbents have been researched and used for boron removal, for instance, fly ash, industrial waste materials, red mud, and waste straw, the study of new type inorganic sorbents for boron such as LDHs, mesoporous silica, zeolites, magnetic nanoparticles, removal has become a hot area of research. Further research is required to make this process more cost effective.

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