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Review

Constructed wetlands for boron removal: A review

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ABSTRACT

Boron (B) contamination in the environment still increases because of various natural sources and anthropogenic activities. Therefore, the problem of removing B from water becomes a worldwide concern due to its toxicity and chronic effects on plants, animals and human health. This situation has generated increasing interest in the use of several wastewater treatment technologies in order to remove B from contaminated water. Constructed wetlands (CWs) present friendly alternative methods to treat wastewater around the world, and are used for removing various contaminants including metals and metalloids. This paper reviews current knowledge regarding the removal process of B, discusses application of B removal, and identifies critical knowledge study fields of future and gaps. Despite the fact that the sediment is a major sink for the removal of B, plants can play a significant role under favorable environmental conditions. The most important environmental factors that affect B removal in CWs are climatic conditions (e.g. transpiration rates), pH, temperature, solutions composition and competing species, hydraulic retention time and supporting media. Further research is needed on the major removal mechanism of B in CWs, namely the applicability of surface flow system, hybrid systems and vertical flow systems to remove B from wastewaters, the role of microorganism in order to enhance B removal efficiency.

1. Introduction

The elevating cost of energy in recent years together with operation cost of wastewater treatment have led to a strong interest to find alternative treatment strategies to conventional technologies (Tu et al., 2010). Constructed wetlands (CWs) represent an eco-friendly alternative for various types of wastewater around the world (Vymazal, 2009). Constructed wetlands are found in Europe, North America, South and Central America, Australia, New Zealand and Oceania, Africa and Asia (Vymazal and Kröpfelová, 2008). Probably more than 100,000 CWs worldwide currently treat over billion litres of water per day (Kadlec and Wallace, 2009; Zhi and Ji, 2012). With the recent rapid growth in wastewater treatment technologies, the issue of boron (B) treatment by CWs has come under the scientific spotlight. In recent years, several laboratory and field experiments have been carried out to determine how CW systems can be applied for B removal (Ye et al., 2003; Murray-Gulde et al., 2003; Kuyucak and Zimmer, 2004; Gross et al., 2007; Allende et al., 2012; Türker et al., 2013a,b). However, the applicability of the CWs is not yet clearly assessed in view of recent findings on B removal.

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In the current paper, B chemistry and behavior in aquatic environments, general B related problems in the aquatic environment and the current knowledge regarding the applicability of CWs to removal of B are reviewed. Boron removal mechanisms in sediment and the role of plants in CWs are also discussed in the review. Finally, data needed for full understanding of possible use of CWs for B removal are presented.

2. Chemical properties of boron

Boron is a metalloid (atomic weight 10.811, solid state 298 K, melting point 2349 K, boiling point 4200 K) in group 13 of periodic table, and it is not found as a free element in hydrosphere and lithosphere. It always binds with oxygen to form both borate minerals (borax, ulexite and colemanite) and orthoboric acid (Gemici et al., 2008; Wolska and Bryjak, 2013). The average B concentration in earth's crust is 10 mg kg^{-1} and varies from 1 to 500 mg kg^{-1} depending on the composition of substrate type (Hilal et al., 2011; Wolska and Bryjak, 2013).

3. Boron related problems in the environment

Soil environment is sensitive to pollutants because many bacterial activities and plants uptake are facilitated by dissolved phases of pollutants in the soil. Boron concentration in the soils varies between 2 and 100 mg kg^{-1}, with an average concentration of 30 mg kg^{-1} (Nable et al., 1997). The high concentrations of B in the soil may be the source of B toxicity effects observed in plants (Camacho-Cristóbal et al., 2008). In the recent years a significant increase in the amount of B in soil has led to decreased plant growth as well as crop yield especially in arid or semi-arid regions (Nable et al., 1997; Miwa et al., 2007).

Boron is relatively soluble in water and commonly causes environmental problems, especially for surface waters where most of the discarded B will end up (Schoderboeck et al., 2011). The most noteworthy problems are in parts of Chile, Turkey, China, New Zealand and many parts of USA (Powell et al., 1997; Ye et al., 2003; Craw et al., 2006; Allende et al., 2012; Türker et al., 2013a). The high solubility of B minerals in water and its potential to cause teratogenic effects have raised global concerns about this element for drinking waters reserves where most of them flow through B-enriched areas. Therefore, World Healty Organization (WHO) recommended 0.5 mg l^{-1} standard for B in drinking water because the poor performance of B removal processes in the treatment technology in areas with high natural B concentrations (Hilal et al., 2011). In 2009, according to the latest data from the UK and USA on dietary intakes, the Drinking-Water Quality Committee recommended the B guideline value of 2.4 mg l^{-1} (Wolska and Bryjak, 2013).

Boron toxicity in plants is an important factor that can limit crop yield and the quality of production in agricultural areas even if it is a micronutrient essential for plant growth (Miwa et al., 2007). The typical symptoms of B toxicity in the crop plants are yellowing of the leaf tips, chlorotic and necrotic patches in the margin/older leaves and spots on fruits (Nable et al., 1997). Boron toxicity has been reported to reduce yield for crop plants in as many as 80 countries in the regions with alkaline soils couple with high pH, as well as soils with strong rainfall leaching regimes (Shorrocks, 1997; Lehto et al., 2010). Boron toxicity in plants is mainly dependent on B concentrations in both irrigation water and soil solution and on B tolerance mechanisms in plants. Therefore, the B concentration should not exceed 4 mg l^{-1} and 10 mg l^{-1} for irrigation water and soil solution, respectively (Nable et al., 1997).

The daily intake of B by animals may vary widely, depending on the different species of animals which showed the effects of B exposure on reduced growth, suppression of male reproductive system function and cutaneous disorders (Ku et al., 1993). Experimental animal studies indicated that the most sensitive endpoints for repeat dose of B are seen on the reproductive system associated with reversible inhibition of spermiation (Scialli et al., 2010). Boron is also trace elements in human's diet and humans need on average 1.4 mg d^{-1} of B in normal diet with average dietary intake (Çöl and Çöl, 2003). However, people living in areas rich in B and who use drinking water supply from B-rich artesian wells may have higher B exposures (Scialli et al., 2010). Excess of B can also be delivered in the human diet through food such as fruit, vegetables and nuts grown in B rich soils and irrigated or contaminated with high concentration B. Çöl and Çöl (2003) indicated that these people can be exposed to chronic B intake thorough both food and water.

4. Boron in water

Boron is found as several species in water depending on their concentrations in water. The main factor that control B speciation is pH (Tu et al., 2010). At higher concentrations at high pH ($\leq$10), polynuclear B species such as $[B_3O_3(OH)_5]^{2-}$ and $[B_4O_5(OH)_4]^{2-}$ are found in the water. However, at low concentrations, mononuclear species boric acid $[B(OH)_3]$, borate ions $[B(OH)_4{}^-]$ or boric oxide (B_2O_3) would be dominant (Hilal et al., 2011). These B species are water soluble and as such are found in surface water system, usually river, lake and ground water (Neal et al., 2010; Schoderboeck et al., 2011). The total concentration of B in water is shown below along with the sum of the two species.

$$[B]_t = [B]_{B(OH)_3} + [B]_{B(OH)_4{}^-} \quad (1)$$

The equilibrium chemistry in water between boric oxide and boric acid species could be described:

$$B_2O_2 \leftrightarrow HBO_2 \leftrightarrow B(OH)_3 \quad (2)$$

In freshwater ecosystems, boric acid accounts for approximately 95% of the dissolved B, whereas the borate ion is approximately 5% (Dotsika et al., 2011). Boric acid is moderately soluble in water and behaves as a very weak Lewis acid. The behavior of boric acid in water systems depends on other parameters such as temperature, pressure, pH and ionic strength (Hilal et al., 2011). Chemical speciation of boric acid varies with acidity according to the flowing equilibrium equation:

$$B(OH)_3 + H_2O \leftrightarrow B(OH)_4{}^- + H^+; \quad pK_a = 9.15 \text{ at } 25\,^\circ C \quad (3)$$

The average B concentration of B in surface water is 0.1 mg l^{-1} (Davis et al., 2002) but higher concentrations can be found in some areas (Schoderboeck et al., 2011). Boron concentrations in surface water range from 10 μg l^{-1} to 200 mg l^{-1} (Okay et al., 1985; Wyness et al., 2003; Böcük et al., 2013). In general, B is relatively easily mobilized during the water-rock interactions (Wolska and Bryjak, 2013). Many studies have shown that the potential B source for surface water and shallow ground water systems are: (i) natural B contamination in surface waters (Çöl and Çöl, 2003; Wyness et al., 2003; Gemici et al., 2008) (ii) fertilizers, herbicides and insecticides (Waggott, 1969; Davidson and Bassett, 1993; Wyness et al., 2003; Hasenmueller and Criss, 2013), (iii) mine waters and wastes (Okay et al., 1985; Neal et al., 1998; Wyness et al., 2003; Böcük et al., 2013; Türker et al., 2013a), (iv) B-enriched detergents and cleaning products released into surface waters through treated and untreated wastewater (Waggott, 1969; Neal et al., 1998; Wyness et al., 2003; Stueber and Criss, 2005; Hasenmueller and Criss, 2013). The use of perborate products increases B concentrations in the domestic wastewater and little or no B is removed during conventional wastewater treatment process (Barth, 2000). The results of domestic wastewater discharge can contribute to elevated B concentration in aquatic habitats (Waggott, 1969; Vengosh et al., 1994; Barth, 2000; Chetelat and Gaillardet, 2005; Hasenmueller and Criss, 2013).

Some industrial wastewaters could be enriched with B with concentrations >1 mg l^{-1}. The major industrial applications are detergents, soap and cleaning products, ceramic, chemical and fertilizer manufacture (Neal et al., 2010). Turek et al. (2007) reported B concentrations between 63.5 and 76.5 mg l^{-1} in industrial landfill leachate from Poland. In the ceramic industry, the wastewater contains 15 mg l^{-1} B and 2000 mg l^{-1} suspended solids (Chong et al., 2009). The boron concentrations of 46.5 mg l^{-1} in electric utility wastewater were reported by Ye et al. (2003). Irawan et al. (2011) reported boron concentration of 745 ± 15 mg l^{-1} in polarizer manufacturing facility in Tainan, Taiwan. Also, concentration of B can be elevated in area of B mining (Türker et al., 2013a). The boron concentrations in mine effluent can reach values of 2000 mg l^{-1} (Türker et al., 2013a,b; Böcük et al., 2013). On the other hand, Murray-Gulde et al. (2003) and Rahman (2009) reported B concentration in oil field produced water as 7 and 28 mg l^{-1}, respectively. These reports comes from literature have showed that CWs could have considerable potential to remove B from both domestic and industrial wastewater.