



Review

Chromium removal in constructed wetlands: A review

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ABSTRACT

The distribution, mobility and availability of metals in the environment depend not only on their total concentration but also on their formations and bounds with the soil. Hexavalent chromium is a very toxic, metal compound, frequently found in polluted industrial wastewaters, and causes serious environmental problems. The potential application of constructed wetlands in the treatment of chromium bearing wastewaters has been reported recently. This paper reviews research on constructed wetlands treating chromium polluted wastewaters, and focuses on several design and operational parameters. The review highlights the effect of vegetation type, hydraulic residence time and porous media type on wetland performance. Constructed wetlands have been proved to be rather efficient at treating chromium containing wastewaters.

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Contents

Introduction	181
Chromium removal mechanisms in CWs	182
The role of vegetation	182
The role of microorganisms	183
CWs for Cr removal	183
Effect of wetland vegetation on Cr removal	185
Typha	185
Phragmites	185
Other plant species	185
Phytotoxicity effects of Cr on wetland plants	186
Effect of porous media on Cr removal	186
Discussion and future research suggestions	187
Conclusion	188
Acknowledgments	188
References	188

Introduction

Chromium (Cr) is the earth's seventh most abundant element, the 21st most abundant metal in the earth's crust, and is mined as

chromite (FeCr_2O_4) (Barnhart, 1997; Cervantes and Campos-Garcia, 2007). In aquatic systems, Cr exists in two oxidation forms: trivalent (Cr(III)) and hexavalent (Cr(VI)) (Barnhart, 1997). While both forms of Cr have been used in different industrial operations, Cr(VI) is mostly used in steel production and chrome plating and Cr(III) compounds are used as leather tanning agents (Altundogan, 2005).

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Cr toxicity is highly dependent on its oxidation form and Cr(VI) is more toxic than Cr(III) for plants, animals and microorganisms. High Cr(VI) concentrations have significant harmful effects on human health including lung cancer, kidney, liver and gastric damage (Nethercott et al., 1994; Cieslak-Golonka, 1995; Wang et al., 1997; EPA, 1998; Kimbrough et al., 1999; US Department of Health and Human Services, 2000). On the contrary, Cr(III) is less toxic to humans and is an essential dietary nutrient (Anderson, 1989, 1997; Katz and Salem, 1994). However, excess quantities of Cr(III) also cause damage to aquatic organism and disrupt the food chain (Bosnic et al., 2000). The maximum permitted discharge level of total Cr into surface and potable waters has been set to below 0.05 mg/L by the Environmental Protection Agency (USA) (Baral and Engelken, 2002) and the European Union (EC, 1998).

Various treatment technologies have been developed for the removal of heavy metals from water and wastewater. Several physicochemical methods are used to remove heavy metals from wastewaters including ion exchange (Pansini et al., 1991; Rengaraj et al., 2001), activated carbon (Perez-Candela et al., 1995; Chingombe et al., 2005; Mohan and Pittman, 2006; Owlad et al., 2009), chemical precipitation (Kongsricharoern and Polprasert, 1996; Ramakrishnaiah and Prathima, 2012), adsorption (Ravikumar et al., 2005; Hashem et al., 2007), reverse osmosis (Perez Padilla and Tavani, 1999), and membrane technologies (Pugazhenthai et al., 2005; Aroua et al., 2007; Muthukrishnan and Guha, 2008). In some cases, these physicochemical processes are extremely expensive especially when the metal concentrations in the solution range from 1 to 100 mg/L (Nourbakhsh et al., 1994). Furthermore, these methods usually produce large quantities of toxic chemical sludge, of which disposal is a major problem (Benjamin, 1983; Mandi et al., 1996).

On the other hand, Cr(VI) interacts with microorganisms through enzymatic reduction, biosorption and bioaccumulation (Tekerekpoulou et al., 2013). Cr(VI) is mainly accumulated by bacteria using the sulfate pathway (Vaiopoulou and Gikas, 2012). Researchers have examined biological Cr(VI) removal using bacteria (Stasinakis et al., 2002; Zouboulis et al., 2004), fungi (Sanghi and Sankaramakrishnan, 2009), yeast (Chen and Wang, 2007), and algae (Bankar et al., 2009). Biological treatment of Cr(VI) is gaining ground due to its very low chemical requirements and operating costs (Srivastava and Majumder, 2008).

Constructed wetlands (CWs) have grown in popularity since the early 1980s (Reed et al., 1995). CWs have been used to treat municipal wastewaters (Vymazal, 2005), acid mine drainage (Machemer et al., 1993; Mays and Edwards, 2001; Yang et al., 2006), industrial wastewaters (Maine et al., 2006; Khan et al., 2009; Di Luca et al., 2011; Kongroy et al., 2012), agricultural wastewaters (Bubba et al., 2004; Nahlik and Mitsch, 2006; Grafias et al., 2010) and tannery wastewaters (Kucuk et al., 2003; Calheiros et al., 2007, 2008a, b, 2010, 2012; Dotro et al., 2011a). These systems are very cost effective compared to conventional wastewater treatment methods (Knox et al., 2006).

Various applications/experiments using CWs for Cr removal have been recorded in the last decade, at both laboratory-scale (Srisatit and Sengsai, 2003; Maine et al., 2006; Mant et al., 2006; Liu et al., 2010; Yadav et al., 2010; Dotro et al., 2011a, b, 2012) and full-scale (Vymazal, 2005; Maine et al., 2007; Khan et al., 2009; Hadad et al., 2010; Di Luca et al., 2011; Kelvin and Tole, 2011). These applications either examine Cr removal from various types of wastewaters (Kucuk et al., 2003; Vymazal, 2005; Mant et al., 2006; Maine et al., 2006, 2007a, 2009; Lesage et al., 2007a; Aguilar et al., 2008; Dorman et al., 2009; Khan et al., 2009; Arroyo et al., 2010; Hadad et al., 2010; Di Luca et al., 2011; Kelvin and Tole, 2011; Dotro et al., 2011b, 2012; Baker et al., 2012; Fibbi et al., 2012; Kongroy et al., 2012; Soda et al., 2012) and activated sludge

(Stefanakis and Tsihrintzis, 2012) or from Cr-containing aqueous solutions (Liu et al., 2010; Yadav et al., 2010; Michailides et al., 2013; Sultana et al., 2014). The extremely high Cr removal efficiencies (up to 100%) achieved in these studies together with their low capital and operational costs, make CWs an attractive alternative for Cr removal. CW is a flexible treatment method, as it can be used as a single treatment step or as a polishing stage in an existing treatment facility depending on the exact specification of the wastewaters concerned.

In the above-mentioned research on using CWs for Cr removal, the effects of a series of operational parameters (i.e., hydraulic residence time, porous media, vegetation etc.) have been examined. To the best of our knowledge, a review summarizing all research results on CWs treating Cr does not currently exist in the literature, therefore this paper fills that gap and summarizes results achieved in CWs treating Cr. This work also discusses the effects of vegetation type, porous media and microorganisms on Cr removal, and toxic effects observed on CW vegetation. Finally, suggestions for future research topics are provided.

Chromium removal mechanisms in CWs

The removal mechanism of heavy metals in constructed wetlands is a complex combination of physicochemical and biological processes including sedimentation, binding to porous media, plant uptake, and precipitation as insoluble forms (mainly sulfides and (oxy-) hydroxides) (Kadlec and Wallace, 2009). The efficient reaction zone in constructed wetlands is the root zone area (rhizosphere) where physicochemical and biological processes take place by the interaction of plants, microorganisms and pollutants (Stottmeister et al., 2003).

The role of vegetation

CW vegetation plays an important role in Cr removal as it (a) releases root exudates which may directly or indirectly impact metal mobility and toxicity; (b) provides large surface area for microbial growth, (c) accumulates Cr in its tissues (Cheng et al., 2002; Southichak et al., 2006; Zhang et al., 2010). The organ of the plant that mainly accumulates metals is the root zone, and this is due to: (a) the slow mobility of metal transport from roots to shoots in vascular plants, and (b) the formation of complex compounds with carboxyl groups which prohibit the translocation of metals to the shoots (Choo et al., 2006; Baldantoni et al., 2009; Zhang et al., 2010). Submerged, rooted aquatic plants withdraw metals from the soil sediments using their root system and accumulate these metals in their belowground biomass (Khan et al., 2009; Fibbi et al., 2012). Zayed and Terry (2003) and Yadav et al. (2005) also state that Cr ions have the ability to bind or precipitate in the cell walls of plant tissue which also limits their translocation. Hence it might be said that accumulation, retention and immobilization of metals in plant roots occur by the rhizofiltration process and that roots are the fundamental site of metal uptake in plants. Consequently, the concentration of metals is higher in roots than other plant parts, while only 2% of the metals are stored in the whole plant biomass (Lee and Scholz, 2007). Moreover, plants contribute to metal deposition in the porous media through rhizodeposition (Kidd et al., 2009). Furthermore plants also act as a catalyst in biochemical reactions between metals and organic acids (e.g. citrate, oxalate, malate, malonate, fumarate and acetate), which due to their anionic form can reduce metal phytotoxicity through the formation of chelate metallic ions (Ryan et al., 2001).

Normally plants receive elements in their ionic forms. Most metal ions enter plant cells by specific metal ion carriers or channels. Within plant cells, Cr ions can form chelating compounds with

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