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Research article

Investigation of kinetics and absorption isotherm models for hydroponic phytoremediation of waters contaminated with sulfate

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ABSTRACT

Two common wetland plants, Pampas Grass (*Cortaderia selloana*) and Lucky Bamboo (*Dracaena sanderiana*), were used in hydroponic cultivation systems for the treatment of simulated high-sulfate wastewaters. Plants in initial experiments at pH 7.0 removed sulfate more efficiently compared to the same experimental conditions at pH 6.0. Results at sulfate concentrations of 50, 200, 300, 600, 900, 1200, 1500 and 3000 mg/L during three consecutive 7-day treatment periods with 1-day rest intervals, showed decreasing trends of both removal efficiencies and uptake rates with increasing sulfate concentrations from the first to the second to the third 7-day treatment periods. Removed sulfate masses per unit dry plant mass, calculated after 23 days, showed highest removal capacity at 600 mg/L sulfate for both plants. A Langmuir-type isotherm best described sulfate uptake capacity of both plants. Kinetic studies showed that compared to pseudo first-order kinetics, pseudo-second order kinetic models slightly better described sulfate uptake rates by both plants. The Elovich kinetic model showed faster rates of attaining equilibrium at low sulfate concentrations for both plants. The dimensionless Elovich model showed that about 80% of sulfate uptake occurred during the first four days' contact time. Application of three 4-day contact times with 2-day rest intervals at high sulfate concentrations resulted in slightly higher uptakes compared to three 7-day contact times with 1-day rest intervals, indicating that pilot-plant scale treatment systems could be sized with shorter contact times and longer rest-intervals.

1. Introduction

Since many industries use sulfuric acid or sulfate-rich compounds in their processes, sulfate has become one of the major constituents of industrial effluents (Guerrero et al., 2013). Industries such as pulp and paper, tannery, mining, smelting, fertilizer producing, textile, and fish and food processing generate considerable volumes of wastewater containing sulfate (Davies, 2007; Tait et al., 2009). Table 1 summarizes sulfate concentration ranges in different industrial effluents.

As seen from Table 1, sulfate concentrations can vary from tens of milligrams per liter to thousands of milligrams per liter, and depending on mass loading rate, could result in significant sulfate concentration elevations above background levels in receiving waters. Global Environmental Monitoring System reported that typical concentration of sulfate range from 0 to 630 mg/L, 2 to 250 mg/L, and 0 to 230 mg/L in rivers, lakes, and groundwaters, respectively (UNEP, 1990).

Chronic exposure of livestock to elevated levels of sulfate may result in weight loss, disease, and death (Iowa-DNR, 2009). Weeth and Capps (1972), reported that 30-day exposure of cattle to water with sulfate concentrations of 1450, 1462, and 2150 mg/L could result in disinclination against high-sulfate water, reduction in weight gain, and rejection of drinking water, respectively. Exposure of cattle to water with sulfate concentrations of 2360 mg/L for 113 days and 2608 mg/L for 54 days, could result in decreased carcass characteristics and body condition, respectively (Loneragan et al., 2001; Patterson et al., 2004). Due to cathartic effects of waters with sulfate concentration of around 500 mg/L on humans and animals, the World Health Organization maintains that health authorities need to be notified if sulfate concentration in drinking

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Table 1
Sulfate concentration ranges in different industrial effluents.

Type of effluent/sample	Reported sulfate concentration (mg/L)	Reference
Tannery wastewater-soaking process	450 ± 30	(Galiana-Aleixandre et al., 2011)
Treated mine wastewater	87.4–596.7	(Silva et al., 2012)
Non-treated laboratory wastewater	263–296	(Benatti et al., 2009)
Contaminated groundwater	851 ± 33	(Chen et al., 2014)
Mine wastewater	588–1100	(Silva et al., 2012)
Sulfate-rich groundwater	957.1 ± 87.1	(Guerrero et al., 2013; Wu et al., 2012)
Sweetmeat waste	1425	(Das et al., 2015)
Rubber latex wastewater	1819 ± 483	(Saritpongteeraka and Chaiprapat, 2008)
Tannery wastewater-unhairing process	2350 ± 179	(Galiana-Aleixandre et al., 2011)
Tannery wastewater-retaining, dyeing, and greasing processes	2360 ± 658	(Galiana-Aleixandre et al., 2011)
Textile	2450	(Kabdaşlı et al., 2016)
Tannery wastewater	1950–8450	(Guerrero et al., 2013)
Tannery wastewater-tanning process	6021 ± 223	(Galiana-Aleixandre et al., 2011)
Pharmaceutical wastewater	7845–8145	(Li et al., 2015)
Copper smelting effluent	49,136	(Basha et al., 2008)
Washing of sulfonated of vegetable oils	201,000 ± 35,000	(Sarti et al., 2009)

waters exceed 500 mg/L (WHO, 2004). The U.S. EPA also recommends that sulfate concentration as a secondary health standard in drinking water be less than 250 mg/L (U.S. EPA, 2009).

Plants take up sulfate and utilize it as a source of sulfur, particularly in the synthesis of the amino acid cysteine (Lunde et al., 2008). Sulfur is regarded as one of the essential macro elements for plants, thus sulfur-deficient plants produce a lower quality and quantity of yield (Wang et al., 2009). However, elevated sulfate concentration is toxic and has growth inhibitory effects on plants (Chandler et al., 1988; Fort et al., 2014; Geurts et al., 2009).

In recent years, phytoremediation, has become popular for remediating a wide range of contaminants (Chen et al., 2014). Although phytoremediation is known as an environmentally friendly and cost-effective method that could effectively comply with the needs in developing countries, due to unfamiliarity and lack of coordination between policy maker and engineers, phytoremediation is not currently a well-adopted method in these countries (Kivaisi, 2001).

Hydroponic or floating aquatic systems and soil-based constructed wetlands are the two main subcategories of phytoremediation systems. Table 2 summarizes the advantages and disadvantages of soil-based constructed wetlands compared to hydroponic systems.

Candidate plants used for phytoremediation purposes should have high uptake rates, high levels of tolerance, high above-ground biomass, easy cultivation, and be extensively competitive compared to other plants growing in the region of interest (Li et al., 2015; Piouceau et al., 2014; Ravanbakhsh et al., 2016). Studies specifically conducted on hydroponic phytoremediation of sulfate are scarce, however research on soil-based systems for the treatment of sulfate containing effluents has shown that plants from *Cyperaceae*, *Araceae*, *Poaceae, Brassicaceae, and Typhaceae* can successfully be used in phytoremediation systems (Chen et al., 2016; Oyuela Leguizamo et al., 2017).

Pampas grass and Bamboo, two common species in natural wetlands, are genera with dense roots from the *Poaceae* and *Agavaceae* families, respectively, that can be used in phytoremediation (Saiyood et al., 2010; Saura-Mas and Lloret, 2005). Pampas grass, known as *Cortaderia selloana*, occurs near river banks and wetlands. They can reach heights of about 2–4 m, diameters between 2 and 3 m, and their root systems can penetrate to a depth of around 3.5 m (Khandare et al., 2011; Robacker, 1995; Saura-Mas and Lloret, 2005).

Previous studies have reported *Cortaderia selloana* to have potential for remediating a variety of contaminants (Couto et al., 2012; Jia et al., 2017; Jiménez et al., 2011). Couto et al. (2012), reported successful treatment of a contaminated soil with refinery effluents by phytoremediation methods using *Cortaderia selloana.* Khandare et al. (2011), found Pampas grass to be able to treat wastewaters containing a wide range of dyes.

Lucky Bamboo *(Dracaena sanderiana)* is an evergreen fast-growing plant, originally a native of Africa, which has practical uses in remediation (Nath et al., 2008; Saiyood et al., 2010). Saiyood et al. (2010), employed *Dracaena sanderiana* for the removal of bisphenol A (BPA) from a synthetic wastewater in a hydroponic system. Sereshti et al. (2014), reported that *Dracaena sanderiana* can be effectively used as a biosorbent for the removal of Hg and Cd from contaminated waters. Their results showed that accumulations of Hg and Cd in plant tissues were 10.32 and 30.90 mg/kg, respectively.

Despite merits claimed in the literature for phytoremediation of sulfate using different plant species including *Arabidopsis thaliana* (*Brassicaceae* family), *Lemna gibba* (*Araceae* family), and *Zea mays (Poaceae* family), only a limited number of studies have reported kinetics of treatment, absorption isotherms, and formulated plants' uptake capacity for contaminant removal (Honda et al., 1998; Khellaf and Zerdaoui, 2009; Nocito et al., 2006). Most prior studies have focused on the interaction of sulfate with heavy metals or other contaminants, or evaluated the physiological and physicochemical parameters of plants' growth (Chen et al., 2014; Davies, 2007; Geurts et al., 2009; Lahive et al., 2011; Nilratnisakorn et al., 2007; Renault et al., 2001; Wiessner et al., 2008, 2010). This

Table 2
Advantages and disadvantages of soil-based constructed wetlands as an alternative to hydroponic systems (Chen et al., 2014; USDA, 2009).

Advantages	Disadvantages
Higher performance of plants due to presence of nutrients in soil.	Higher capital cost.
Higher overall treatment efficiency due to synergistic effects of other treatment mechanisms including phytostabilization, rhizofiltration, and bioremediation.	Require pre-treatment processes to prevent clogging.
Less water loss due to evaporation.	Require irrigation water distribution systems to avoid short circuiting.