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Using indigenous microalga species to reduce HCO_3^-, NH_3N, NO_3N, total P, Ca^{2+}, SO_4^{2-}, and Cl^- from a high conductivity concentrate

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HIGHLIGHTS

- Dissolved ions were degraded by natural species from concentrate evaporation pond.
- Initial microalgae-to-conductivity ratio (M/C) was 0.0008 to 0.001 g/(L μS/cm).
- Conductivity reduction (R) was 27.6–33.6% in 15 days. R is directly linear with M/C.
- R of HCO_3^-, NH_3N, NO_3N, and total P was 83.9–88.0, 69.0–77.6, 63.6–57.1, and 59.1–70.7%.
- R of Ca^{2+}, SO_4^{2-}, and Cl^- was 47.3–59.4, 12.6–19.0, and 6.3–18.2%, respectively.

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ABSTRACT

Natural microalga species from desalination concentrate evaporation pond was used to reduce dissolved ions from a high level conductivity of desalination concentrate and leachate of anaerobic digested sludge (LADS) compost. The initial microalgae-to-conductivity ratio was in the range of 0.0008 to 0.0010 g/(L μS/cm). LADS was supplied as nutrients. Carbon dioxide from the environment was dispersed into the growth medium. Mass conductivity reduction (Y) of 27.6–33.6% was achieved in 15 days. Y is directly linear with mass microalgae-to-conductivity-ratio (X) as Y = 30930X + 8.9182 with R^2 0.996: $p < 0.001$ in three different studies with two different species. Reduction was on the order of HCO_3^-, NH_3N, NO_3N, total P, Ca^{2+}, SO_4^{2-}, non-Ca^{2+} and multi-valent cations, and Cl^- with mass reduction percentage 83.9–88.0, 69.0–77.6, 63.6–57.1, 59.1–70.7, 47.3–59.4, 12.6–19.0, 4.5–24.5, and 6.3–18.2, respectively. Reduction sequence follows C, N, P, Ca^{2+}, SO_4^{2-}, and Cl^- as primary-, macro-, and micro-nutrients of microalga composition. Carbon species, $H_2CO_3^*$ was dominant in the growth medium.

1. Introduction

Because of climate change, the Southwest United States is suffering significant drought, and all fresh surface water resources are gradually diminishing. Humans, livestock, and crops in these regions are now reliant on fresh water resources other than surface waters. Agriculture consumes more than half (70%) of the extracted groundwater. Agriculture will need 19% more water by 2050 because of the increasing trend of world population. Normally, groundwater is brackish with dissolved ions, and not fit for human drinking, livestock watering, or crop irrigation. Reverse osmosis and electrodialysis are the typical desalination technologies used to convert brackish groundwater into drinking water. However, these technologies discharge about 30% of input brackish groundwater as waste concentrate, and this waste is usually disposed directly or indirectly back into the air, the ground, and the sea. The disposed waste concentrate naturally contaminates the air, water, and soil. To avoid and reduce this contamination, desalination concentrate was reused along with leachate from compost of sludge as growth medium to grow microalgae (*Dunaliella salina* and *Spirulina platensis*) for protein and desalted water for animal by Hussein et al. [1]. Desalination concentrate contains dissolved HCO_3^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, S^{2-}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, K^+, Na^+, and other minerals that are substrates, macro- and micro-nutrients for the microalgae to grow as stated in Pruvost et al. [2] and Goldman et al. [3] if microalgae receive proper light energy, carbon, and nutrients.

To produce a high yield of useful product, microalgae require an adequate carbon and nutrient, light, operational and environmental conditions. Temperature and light irradiance are the key factors that influence biomass composition, and dry weight loss during the night is due to the decrease of these two factors as stated in Torzillo et al. [4]. Elemental composition of microalgae also depends on the feed

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compositions as stated in He et al. [5] and environmental conditions as stated in Olguín [6]. Constant pH in growth medium is also required in microalga production, since pH fluctuations can be harmful to aquatic systems. A fluctuation of pH can be minimized by supplying and maintaining dissolved CO_2 in alkaline HCO_3^- species. HCO_3^- acts as a buffer to protect the growth medium from pH fluctuations as stated by Whipple [7]. Another way to minimize the fluctuation of pH is to add leachate from anaerobic digested sludge compost which has a considerable amount of alkalinity (1485 mg/L as $CaCO_3$, Stdev 40). To reduce costs and environmental burdens, all above requirements must come from economical or free pollution sources as stated in Chisti [8].

An open pond tends to have species contamination, water loss from evaporation, and suffers from temperature swings between day and night periods. Microalgae working well in the lab did not demonstrate well in the field as stated in Sheehan et al. [9] due to the different conditions between lab and field. Microalga biomass losses during the night were due to decrease of temperature and light irradiance as stated in Torzillo et al. [4]. Natural concentrate from desalination has to be tested to assure close simulation of real world condition as stated in Visvanathan et al. [10] and to reduce the disconnection between lab and field.

Indigenous microalgae naturally grown in desalination concentrate from an evaporation pond were used as seed in Myint, DWT-2014-0281 [11] studies to reduce the dissolved ions from natural desalination concentrate as recommended by Olguín [6]. The overall mass conductivity reductions from natural concentrate and nutrients were 54.7, 53.4, 45.8, 37.3, and 40.4% from the initial mass conductivities (52,904, 66,214, 82,229, 106,662, and 122,432 L μS/cm, respectively), in 110 days of treatment in Myint, TDWT-2014-0281 [11]. One undesirable aspect of Myint's TDWT-2014-0281 [11] experiment is the required length of treatment time or the large required surface area of the reactor. The highest mass densities of microalgae in the growth cultures were 1.63 to 2.17 g/L (dry), and the conductivities of growth cultures were 24,000 to 59,800 μS/cm. The mass densities of microalgae were very small when compared to the mass conductivities of the growth culture.

Hyper-concentrated cultures of microalgae — *Scenedesmus obliquus* (up to 2.6 g L^{-1} dry) were used in the laboratory to enhance the reduction of nitrogen and phosphorus concentrations from secondary effluent of the wastewater treatment plant and to reduce the surface area requirement of treatment pond as stated in Lavoie and De la Noüe [12]. *D. salina* with a higher mass microalgae-to-conductivity ratio (0.00027 and 0.00034 g/(L μS/cm)) was used to enhance the treatment of desalination concentrate containing conductivity 30,200–51,800 μS/cm in Myint's EES-2013-0298 [13] experiments. The mass conductivity consumptions were 25.1 and 29.4% by *D. salina* with 0.00027 and 0.00034 g/(L μS/cm) of microalgae-to-conductivity ratio in 21 days of treatments as stated in Myint, EES-2013-0298 [13]. However, detailed analyses of mass reduction from individual ion were beyond the scope of Myint, EES-2013-0298 [13].

2. Hypotheses

Microalgae are capable of reducing heavy ions as stated in Muñoz and Guieyssea [14] and may have the ability to reduce light ions. Reducing light metal ions from desalination concentrate may be improved by using native indigenous species, higher mass microalgae-to-conductivity ratio, and an appropriate treatment time. By integrating the native species naturally grown in desalination concentrate with much higher mass microalgae-to-conductivity ratio, the mass conductivity reduction from concentrate may further decrease the treatment time. The objective of this article is to study the feasibility of individual dissolved ion (HCO_3^-, SO_4^{2-}) reduction by the much higher mass ratio of microalgae-to-conductivity with indigenous autophotrophic species naturally growing in concentrate from evaporation ponds.

3. Method

The experiments were performed with two different ratios of mass microalgae-to-conductivity in clear glass reactors R1 and R2 (3.7 L total volume of each). The reactor configuration and lighting conditions were described in details in Myint, EES-2013-0298 [13]. The initial and final contents of conductivity, microalgae, and mass microalgae-to-conductivity ratio are shown in Tables 1 and 2, respectively. Microalgae from Myint's TDWT-2014-0281 [11] experiment were seeded in reactors R1 and R2 after settling the microalgae and decanting the water. These microalga species of Myint, TDWT-2014-0281 [11] were originally sampled from concentrate in evaporation ponds located in the Brackish Groundwater National Desalination Research Facility (BGNDRF), Alamogordo, NM, USA. These species were named as *BGNDRF species*.

Two light bulbs, 23 W each of CFL/bombillos (Utilitech) were used in the first three days with the light radiation of 110, 82, 125, and 91 μmol m^{-2} s^{-1} in the four measurement points. The light bulbs were increased to four on the fourth day for the rest of the experiment with the light radiation of 332, 336, 378, and 416 μmol m^{-2} s^{-1} as shown in Myint, EES-2013-0298 [13]. Lighting was supplied continuously during the experimental period. Compost from anaerobic digested sludge was collected from the Wastewater Treatment Plant in Las Cruces, NM. Desalination concentrate was collected from desalination concentrate ponds in BGNDRF. Desalination concentrate and leachate from anaerobic digested sludge compost were centrifuged in 50 mL tubes for 3 min at 10,000 rpm, separately. The supernatants were collected as desalination concentrate and leachate, separately. Before centrifuging, 1 kg of compost from anaerobic digested sludge was soaked in 14 L of deionized water for three days, and leachate was separated from the mixture in a centrifuge.

The light radiation was measured with an Apogee MQ-200 PAR meter, USA. The dry weight of microalga concentration, optimal density (OD), and microscopic images, depicted in hemocytometer (or haemocytometer or counting chamber) were used to identify microalga growth. Total suspended solids were measured and used to estimate microalga concentration (dry) according to SM 2540D as stated in APHA [15] and Valigore et al. [16]. Optical density was measured with the Hach DR/2010, USA spectrophotometer at 560 nm wavelength. A microscopic image was observed with a microscope model N-400M. The pH was measured with a Cole Parmer pH meter AB15, USA. The conductivity was measured with a Hach sension5, USA conductivity meter. Ca^{2+}, total hardness, calcium hardness, NH_3N, NO_3N, Cl^-, total alkalinity, and SO_4^{2-} were measured with Hach methods. Non-Ca^{2+} and multi-valent cation percent reduction was calculated from non-calcium hardness. The non-calcium hardness was calculated by total hardness minus calcium hardness. HCO_3^- was calculated from stoichiometric Eq. (4) which is the sum of Eqs. (1)–(3). Reactors were filled with seed microalgae as shown in Table 1. Initial and final contents are shown in Tables 1 and 2. Initial dissolved concentrations in growth mediums in reactors R1 and R2 are shown in Table 3. 60 mL supernatant of desalination concentrate and 200 mL supernatant of leachate from anaerobic digested sludge compost were filled into the reactors every three days at day-0, -3, -6, -9, and -12 as fed-batch reactors. CO_2 from air was supplied in all reactors through three supplying pipes (inner diameter 0.125 in.) continuously during the experimental period. Air supply rate from each pipe was 1.2695 L/min.

$$H_2O + CO_{2(gas)} \leftrightarrow H_2CO_3^* \tag{1}$$

(pH 6.5–7.5; Whipple [7])

$$H_2CO_3^* \leftrightarrow H^+ + HCO_3^- \tag{2}$$