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Microalgal process for treatment of high conductivity concentrates from inland desalination

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ABSTRACT

Desalination concentrate contains high levels of dissolved ions such as alkalinity, sulfate, and synthetic chemicals. Microalgal species that have ability to grow in the presence of these ions can be used to treat concentrates. A natural indigenous microalgal consortium originally grown in the concentrate of an evaporation pond was selected, cultured, and seeded in the growth medium for treatment of concentrates. Fed-batch experiments were performed with five different conductivities of concentrates in five reactors, with duplicates. Supernatants or leachates from anaerobic digested sludges were supplied as nutrients. Energy was supplied by sunlight during regularly scheduled office hours. Artificial light was supplied as energy during the weekend and all holiday hours. Environmental air was supplied as carbon during the office hours, weekend, and holidays. Water quality from treated concentrate in reactor R1 at 20 d of treatment was sufficiently pure to be given to sheep. Overall mass conductivity reductions from concentrate and supernatant or leachate were 54.7, 53.4, 45.8, 37.3, and 40.4% at 110 d for reactors R1-R5, respectively. These reductions depend on the initial conductivity of concentrate. Mass reduction percentage is inversely proportional to initial mass conductivity, with a variation of the coefficients "a" and "b" as a second-order of polynomial function of the treatment time.

Keywords: Natural microalgal consortium; Alkalinity; Anaerobic digested sludge; Brackish Groundwater National Research Facility microalgal species; Dissolved conductivity reduction

1. Introduction

1.1. A natural microalgal consortium

Pressure-driven membrane filtration and electrodialysis (reversal) technologies are popular desalination technologies for drinking water, but these technologies have a drawback in large-scale systems applications because dissolved ions are physically transferred from one stream to another stream. The transferred ions in desalination concentrate needs further treatment, recovery, or reuse since the conventional disposal technologies such as sanitary sewer discharge, evaporation ponds, deep well injection, or land irrigation,

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and ocean disposal are considered unsustainable. These technologies do not capture and reuse all harmful dissolved ions such as phosphates, arsenic, and nitrate. These technologies require high energy to transfer harmful dissolved ions from input feed stream into concentrate stream to produce a product with a sufficiently lowered amount of dissolved ions to meet the drinking water standards. The concentrate stream with high dissolved ions are usually discharged back into the sea or injected into ground or evaporated in evaporation pond. The unwanted ions from concentrates are diluted back into receiving water bodies that are also the original sources of input feed water for desalination as stated by Kumar et al. [1].

In arid regions, open ponds are best suited to treat desalination concentrate by microalgae. To be successful, a natural indigenous microalgal consortium able to grow in desalination concentrate is required as stated by Dragone et al. [2] and Samorì et al. [3] because the desalination concentrate contains high levels of conductivity, alkalinity, sulfate, and synthetic chemicals. In the classical electrodialysis reversal, dimenand velocities of diluted sions, flows, and concentrated waters are equal. Langelier saturation index (LSI) and CaSO₄ saturation level are used to control the scaling and fouling processes in concentrate as such LSI < +2.16 for preventing CaCO₃ from fouling and CaSO₄ saturation level <200 for averting CaSO₄ from precipitation. If LSI is more than the allowable limit, synthetic chemical (acid) is added to the concentrate to keep CaCO₃ to continue to dissolve. If CaSO₄ saturation level in concentrate is more than the allowable limit, sodium synthetic chemical (hexametaphosphate) is added in the concentrate to maintain CaSO₄ to continue to dissolve (Myint et al. [4]). A growth medium with a high alkalinity and high pH (8.5–11.0) is suitable for Spirulina to grow as stated in Habib et al. [5]. A growth medium with high salinity is suitable for Dunaliella salina. A desalination concentrate contains high levels of alkalinity, sulfate, and total dissolved solid (TDS). Utilizing an adapted species is required either by acclimation or by isolating it from desalination concentrate where indigenous species have already been adapted to the target contaminants as primary and secondary nutrients as stated by Malik [6] and Muñoz and Guieyssea [7]. Using species already present in desalination concentrate from an evaporation pond is required to maintain agreement between the lab and the field as stated in Sheehan et al. [8]. The laboratory experiments require conditions for the field condition as such by encouraging an adapted native species already in the evaporation pond to capture and reuse the dissolved ions from the desalination concentrate.

1.2. Low-cost growth medium and nutrients

Biodiesel from microalgae is viewed in the literature as the third-generation of biofuel (Dragone et al. [2]), having advantages over the first- and second-generations (methane and bio-hydrogen biogas and ethanol) of biofuel. However, selecting the right species, maintaining high required quality product (lipid and/or protein), establishing an energy efficient extraction method, and recovering energy and nutrients from the oilcake as stated in Lardon et al. [9] are required to lower the production cost. The reuse of low-cost water medium, nutrients, and other required materials from waste could also reduce significantly the operating costs of microalgae production (Olguín et al. [10] and Costa et al. [11]). The reuses of desalination concentrates and supernatants from anaerobic digested sludges (SADS) and leachates from compost of anaerobic digested sludges (LADS) in microalgal production follow the eco-environmental fundamental. Conservation environmentalists investigate the fundamentals of eco-environmental practices to determine initial specific standards and best practices for achieving the highest harvests with the lowest environmental impact.

1.3. Hypothesis

Microalgal biomass has ability to bio-accumulate manganese dioxide and heavy metal as stated in Hart and Madgwick [12], Boshoff et al. [13], Muñoz and Guieyssea [7]. Concentrates from brackish groundwater desalination contains high amounts of dissolved ions such as sulfate and bicarbonate. Microalgae consume dissolved inorganic carbon as a primary carbon source and nitrate, phosphate and sulfate as nutrients with the right species as stated in Pruvost et al. [14]. HCO_3^- is one of the components of alkalinity and provides more stable microalgae cultures for biofuel production (Gardner et al. [15]). Desalination concentrates from brackish groundwaters could be treated by an adapted native microalgal species with biotransformation of bicarbonate and sulfate (Samorì et al. [3]) into microalgal cells. The objective of this article is to study the feasibility of a natural microalgal consortium which can treat desalination concentrates by reusing SADS or LADS as nutrients.

2. Method

Desalination concentrates and a natural indigenous microalgal consortium were collected from desalination concentrate evaporation ponds of Brackish Groundwater National Desalination Facility (BGNDRF) located in Alamogordo, NM, USA. The species were acclimated to SADS as nutrients for three months. Anaerobic digested sludges and composts from anaerobic digested sludges were collected from the Las Cruces Wastewater Treatment Plant. Desalination concentrates, anaerobic digested sludges, and LADS were centrifuged twice separately at centrifugal force as $11,500 \times g$ for 3 min to separate and collect the supernatant. These supernatants were used in all experiments. The centrifuge was supplied by Eppendorf AG 22331 Hamburg, Germany serial # 5884ZP861228.

2.1. Design of experiment/contents in reactors

One kilogram of compost from anaerobic digested sludge was soaked in 14 L of deionized water for three days at room temperature, and leachate was separated from the mixture in the centrifuge. Next, five different levels of conductivities of concentrates and the acclimated natural indigenous microalgal consortium were poured in five different reactors duplicated, making ten reactors total. The initial conductivities of SADS, LADS, and desalination concentrate are shown in Tables 1 and 2. The initial volume of SADS, LADS, desalination concentrate, and seed microalgae used in each reactor are shown in Table 2. Used bottles (dimensions $14.5 \times 14.5 \times 18 \text{ cm}^3$) were used as reactors. There was no control (samples without microalgae) in the design of the experiments. The initial volume of growth mediums in the reactors including initial volume of desalination concentrate and seed volume of microalgae as shown in Table 2. The initial volume of growth mediums in the reactors R11, R12, R21, R22, R31, R32, R41, R42, R51, and R52 were 2.22, 2.25, 2.24, 2.22, 2.09, 2.09, 2.22, 2.24, 2.12, and 2.12 L as shown in Table 2, respectively. The volume of growth mediums in the reactors R11, R12, R21, R22, R31, R32, R41, R42, R51, and R52 at day 48 were 2.086, 2.170, 2.117, 2.075, 2.012, 2.075, 2.096, 2.096, 2.138, and 2.254 L, respectively. The volume of growth mediums in the reactors R11, R22, and R41 at day 110 were 1.547, 1.648, and 2.532 L, respectively. The volume of growth mediums in the reactors R31, R32, R51, and R52 were 1.782, 1.987, 1.919, and 2.441 L at day 110, respectively. There is no data for reactors R12, R21, and R42 from day 50 to 110. Data were average of two from day 0 to 48 for all reactors. Data were average of two for reactors R31, R32, R51, and R52 from day 50 to 110. Data were without duplicate (without average of two) for reactors R11, R22, and R41 from day 50 to 110.

All reactors were bubbled with the same flow rate of air (828 mL/min) during regularly scheduled office hours from day zero to the end of the tests. All reactors were directly exposed to the sunlight during regularly scheduled office hours by shifting the reactors outside in the day-time and moving them back into the lab room in the night-time. The reactors were irradiated with light bulbs and bubbled with environmental air on holidays and weekends. As shown in Fig. 1, 0.33 L of SADS was fed into each reactor every ten days from 0 to 90 d, and 0.33 L of LADS was fed into each reactor at 100 d as a fed-batch culture. If the addition of SADS or LADS fell on a weekend or a holiday period, these were added at the end of the day just prior to the holiday interval, or in the case of the weekend, at the end of the work on friday.

2.2. Samples analyses

Total solids were measured and used to estimate microalgae concentration (dry) according to SM 2540D as stated in APHA [16] and Valigore et al. [17]. Conductivity was measured with a conductivity meter (Hach sensION5, USA). The pH was measured with a Cole Parmer pH meter AB15 accumet (USA).

3. Results

The average temperature (°C) of the culture inside the bioreactors 1–5 was $25.8^{\circ}C \pm SD \ 0.25$ (n = 10) as they were all cultivated in identical environmental conditions in the laboratory. That temperature in incubations under sun outside was $41.0^{\circ}C \pm SD \ 0.52$ (n = 10). Fig. 1 shows pH of the growth medium as a function of time. Fig. 2 shows mass conductivity reduction percentage from concentrate and SADS or

Table 1

The initial conductivity of supernatant and leachate from anaerobic digested sludge

Type of nutrients	No. of sample	Initial conductivity (µS/cm)	SD
Supernatant from anaerobic digested sludge	16	5,188	229
Leachate from compost of anaerobic digested sludge	16	7,824	340

Notes: Supernatant from anaerobic digested sludge was supplied from day 0 to 100 treatment. Leachate from compost anaerobic digested sludge was supplied from day 110 to the end of test.

The design of experiment for initial conditions, initial conductivities, initial concentrate volume					
Reactor R	Initial conductivity of desalination concentrate µS/cm	Initial volume of desalination concentrate L	Seed volume of microalgae L	Initial total volume of growth medium L	
R11	24,000	2.12	0.1	2.22	
R12	24,000	2.15	0.1	2.25	
R21	30,250	2.14	0.1	2.24	
R22	30,250	2.12	0.1	2.22	
R31	40,500	1.99	0.1	2.09	
R32	40,500	1.99	0.1	2.09	
R41	49,200	2.12	0.1	2.22	
R42	49,200	2.14	0.1	2.24	
R51	59,800	2.02	0.1	2.12	
R52	59.800	2.02	0.1	2 12	

(1)



Fig. 1. pH of growth medium vs. treatment time.

Notes: Data were average of two from day 0 to day 48 for all reactors. Data were average of two for reactors R31, R32, R51, and R52 from day 50 to day 110. Data were without duplicate (without average of two) for reactors R11, R22, and R41 from day 50 to day 110. All reactors were directly exposed to the sunlight during regularly scheduled office hours by shifting the reactors outside in the day-time and moving them back into the lab room in the night-time. The reactors were irradiated with light bulbs on holidays and weekends.

LADS vs. treatment duration. Fig. 3 shows comparison between measured and predicted mass of conductivity reduction from concentrate and SADS or LADS vs. initial mass conductivity (IMC) from concentrate. The relation between mass conductivity reductions from concentrates and SADS or LADS and initial conductivity were found to be inversely linear as:

Mass conductivity reduction percentage

$$= a - b$$
 (initial mass conductivity)



Fig. 2. Mass conductivity deduction percentage from concentrate and SADS (LADS) vs. treatment time. Notes: Data were average of two from day 0 to day 48 for all reactors. Data were average of two for reactors R31, R32, R51, and R52 from day 50 to day 110. Data were without duplicate (without average of two) for reactors R11, R22, and R41 from day 50 to day 110.

The coefficients a and b were found to have a second-order of polynomial function with the treatment time as:

$$a = -0.0028825782 t^{2} + 0.9354261346 t$$

$$-2.8442917279 : R^{2}0.989, n = 10$$
(2)

$$b = -0.000000123 t^{2} + 0.0000037677 t$$

-0.0000374411 : R²0.957, n = 10 (3)

Table 2



Fig. 3. Measured (points) and predicted (lines) mass of conductivity reduction from concentrate and SADS (LADS) vs. IMC from concentrate (Data were the average of two reactors).

Table 3 Coefficients in relation between mass conductivity reduction and IMC

Day	а	b	R^2	п
9.9	7.29	0.000008	0.093	10
19.9	12.49	0.000011	0.138	10
29.8	22.65	0.000070	0.878	10
40.1	28.85	0.000089	0.725	10
49.9	39.21	0.000131	0.923	10
60.0	43.44	0.000154	0.967	10
69.9	48.54	0.000164	0.845	10
79.9	53.52	0.000187	0.855	10
99.9	57.84	0.000184	0.832	10
109.9	67.89	0.000251	0.868	10

Notes: Mass reduction, % = a - b [IMC]. IMC = initial mass conductivity, L µS/cm. n = number of measurement = 5 data with duplicate.

The values of "*a*" and "*b*" are shown in Table 3 as a function of treatment time. The number of total measurement was ten (n = 10) which is five data points with duplicates. Fig. 4 shows the quality of predicted mass reduction against measured value with R^2 . Fig. 5 shows justification of relation between microalgal growth and mass conductivity reduction with time. Fig. 6(a)–(j) show the densities of microscopic images depicted in counting chamber at 110 d of culturing period in reactors R11, R12, R21, R22, R31, R32, R41,

Table 4Cell counts and biomass cell concentrations

Reactors	Biomass cell counts, <i>n</i>	Biomass cell concentrations, cells/mL
R 1-1	15	58,666,667
R 1-2	6	25,333,333
R 2-1	5	18,666,667
R 2-2	4	14,666,667
R 3-1	5	20,000,000
R 3-2	7	26,000,000
R 4-1	5	19,333,333
R 4-2	3	12,666,667
R 5-1	6	23,333,333
R 5-2	4	14,666,667



Fig. 4. Comparison of measured and calculated mass conduction reduction.

R42, R51, and R52. Fig. 7 shows the evolution of conductivity in growth medium over time.

4. Discussion

4.1. The pH of the growth medium

The pH of growth mediums fluctuated from 9.2 to 7.7. The pHs fluctuated sharply immediately after adding SADS or LADS. In all reactors, the pH in the growth medium decreased slightly over time as shown in Fig. 1. The average pH values in reactors 1, 2, 3, 4, and 5 were 8.49 (SD 0.31), 8.52 (SD 0.32), 8.55 (SD 0.26), 8.56 (SD 0.22), and 8.56 (SD 0.20), respectively.



Fig. 5. Relation between microalgae growth and mass conductivity with time (MM = mass microalgae, dry in growth media. T = treatment time, day).

The slightly decreasing trends of pH show that the available dissolved CO_2 in the growth medium is more than the uptake rate of microalgae.

4.2. Mass conductivity reduction

The mass conductivity reductions from concentrates and SADS or LADS in growth medium as a function of treatment time are shown in Fig. 2. The overall mass of conductivity reductions (average of two reactors) from concentrates and SADS or LADS were 54.7, 53.4, 45.8, 37.3, and 40.4%, respectively, in 110 d of treatment as shown in Fig. 2. The least IMC shows the highest mass conductivity reduction percentage from concentrate and nutrient supplied, as shown in reactor 1 of Fig. 2. The largest and the second largest initial mass conductivities show the least mass conductivity reduction percentages from concentrate and nutrient supplied, as shown in reactors 4 and 5 of Fig. 2. The reason for this difference is that the seed-microalgae-to-initial-mass conductivity ratio in reactor 1 was higher than that in reactors 2, 3, 4, and 5 as shown in Table 2. Mass conductivity reduction percentage from concentrate and nutrient decreased with the increase in IMC as shown in Fig. 3.



Fig. 6. The density of microscopic images depicted in hemacytometer (counting chamber) at 110 d of culturing period.



Fig. 7. Change in conductivity growth medium in reactors as a function of time.

The calculated trend of these reductions is inversely proportional to the initial mass conductivities in growth medium (52,904, 66,214, 82,229, 106,662, and $122,432 L \mu S/cm$) as shown in Fig. 3. The calculated mass reductions correlates well with the measured values with R^2 0.983 (Fig. 4). Mass conductivity reduction percentages with respect to IMC were similar at the beginning of the test in 0-20 d of treatment in all five reactors (Fig. 3) because the dry masses of microalgae were similar in all reactors as shown in Fig. 5. Mass conductivity reduction percentages were significantly different with respect to IMC in 40-110 d of treatment as shown in Fig. 3 because the dry masses of microalgae were significantly different from the growth in all reactors as shown in Fig. 5. The dry mass microalgae slowly increased from day 0 to 20 in all reactors as shown in Fig. 5. The rates of dry masses microalgae increased from day 30 as shown in Fig. 5.

Fig. 6(a) and (b) show the highest density of microscopic image in the least initial conductivities of 24,000 and $24,000 \,\mu\text{S/cm}$, respectively. Fig. 6(i) and (j) reveal the lowest density of microscopic image in the maximal initial conductivities of 59,800 and 59,800 µS/cm, respectively. The densities of microscopic images decrease from Fig. 6(a) and (b) to (c) and (d), (e) and (f), (g) and (h), (i) and (j) where the initial conductivities of desalination concentrate increase from Fig. 6(a) and (b) to (c) and (d), (e) and (f), (g) and (h), (i) and (j). Conductivities of culture in 110 d of treatment were significantly less than that of initial desalination concentrate as shown in Fig. 7. Table 4 shows the biomass cell counts and biomass cell concentrations in the reactors R11 to R52, respectively at 110 d of treatment. The biomass cell counts and concentrations decreased with the increase of the initial conductivities of desalination concentrates as shown in Tables 2 and 4.

4.3. Behavior of mass of conductivity reduction percentages

There are several different slopes in mass of conductivity reduction from concentrate and nutrient in all reactors (Fig. 3 and Table 3) with respect to IMC or reactors. There are small reduction slopes [b = -0.000095%] $(L \mu S/cm)$] with respect to original mass conductivity (reactors) during the first period of treatment time of 10-20 d. This means the mass reductions from all reactors 1-5 were not significantly different. The negative slopes reductions with respect to original mass conductivity (reactors) started to increase slightly in 30-40 d of treatment $[0.000070-0.000089\%/(L \mu S/cm)]$ and the slope increased rapidly in 50-110 d [0.000131- $0.000251\%/(L\,\mu\text{S/cm})$]. This means the mass reductions began to vary among these five reactors from 30 to 40 d of treatment, and after that period the differences between reactors are significantly higher in 50-110 d of treatment.

4.4. Usefulness

The desirable TDS and maximum TDS for drinking water quality guidelines for sheep are 5,000-10,000 mg/L TDS or $10,000-20,000 \mu$ S/cm. The range for beefcattle is 4,000-5,000 mg/L TDS or $8,000-10,000 \mu$ S/cm as stated in NSW Public Works [18]. The conductivity from R1 at 20 d of treatment is lower than the conductivity requirement in the drinking water quality guidelines for sheep as shown in Fig. 7. The treated desalination concentrate contains green food as microalgae, protein, nutrients, minerals, and desalted water; the treated desalination concentrate at 20 d of treatment from R1 can be given to sheep by mixing with dry food stock in the semi-arid and arid regions where green food and water availabilities are gradually diminishing.

4.5. Justification of the relation between biomass growth and mass conductivity

Justification of the relation between biomass growth and mass conductivity from concentrate and nutrient is graphically shown in Fig. 5. There is a change in mass conductivity in Fig. 7 between SADS additions because mass conductivity of SADS was added into the growth medium. Overall mass conductivity decreased along with the mass dry weight of microalgae increase in all reactors 1–5 as shown in Fig. 5(a)–(e), respectively. The highest mass dry weight was found in the least IMC as shown in Fig. 5(a). The least mass dry weight was found in the largest IMC as shown in Fig. 5(e). Microalgal growth may have been inhibited from the higher IMC due to the lower initial-mass-microalgaeto-initial-mass conductivity ratio.

4.6. Limitation

SADS or LADS was supplied every 10 d as nutrients. Sunlight or artificial light was supplied as energy during regularly scheduled office hours or weekend and all holiday hours, respectively. Environmental air was supplied as a carbon source during the office hours, weekend, and holidays. The desalination concentrate was supplied only at the beginning of the experiment. The pH of growth medium decreased slightly with the treatment period as shown in Fig. 1. The reason for decrease was that the supply rate of carbon dioxide was higher than the utilization rate by microalgae. Dissolved ions from concentrate may inhibit or limit the growth of microalgae since the trends of microalgal mass decreased with the increasing mass conductivity. The IMC from concentrate was used as an evaluation of the limiting substrate in the model as shown in Eq. (1).



Fig. 8. Linear mass MGR with IMC of concentrate.

4.7. Linear mass growth rate of microalgae

The linear mass microalgae growth rate (MGR) was calculated for microalgae in each reactor as shown in Fig. 5 as 0.074, 0.044, 0.039, 0.032, and 0.027 g/d, respectively. The linear MGR decreased with the increasing IMC as a linear function [MGR = -6E(-07) IMC + 0.091: R = 0.769] and as logarithmic function [MGR = $-0.049 \ln(IMC) + 0.596$: R = 0.844] as shown in Fig. 8.

4.8. Reducing the duration of the treatment

The duration of treatment time may be reduced by increasing the initial microalgae-to-concentrate-ratio and maintaining consistent temperature between the day and night period. This can be accomplished by increasing the seed microalgae in the growth medium. This increase in seed microalgae will lower the conductivity-to-microalgae-ratio. This low conductivity-to-microalgae-ratio will lead to less inhibition from conductivity compared to higher conductivity-tomicroalgae-ratio and may accelerate the MGR. Maintaining consistent temperature may prevent microalgae weight loss during the night period.

5. Conclusion

Dissolved ions from desalination concentrate can be captured and reused by the natural microalgal consortium from concentrate evaporation pond by using SADS or LADS. The overall mass conductivity reduction percentages (average of two reactors) from concentrate and SADS or LADS were 54.7, 53.4, 45.8, 37.3, and 40.4%, respectively, in 110 d treatment. The reductions trends are inversely proportional to original mass of conductivities in 30–110 d of treatment and medium. Water quality of treated desalination concentrate after 20 d of treatment from reactor R1 is sufficient to be given to sheep.

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