

# Large scale phycoremediation of acidic effluent from an alginate industry

V. Sivasubramanian\*, V.V. Subramanian, B.G. Raghavan, R. Ranjithkumar

Vivekananda Institute of Algal Technology, Ramakrishna Mission, Vivekananda College, Chennai 600004, India

\*Corresponding author, e-mail: vsivasubramanian@gmail.com

Received 29 Nov 2008

Accepted 16 Jul 2009

**ABSTRACT:** The present study deals with the successful commissioning of a phycoremediation plant to treat the acidic effluent from an alginate industry. The liquid effluent is highly acidic. Conventionally, sodium hydroxide has been used for the neutralization of the acidic effluent which results in an increase in total dissolved solids and the generation of solid waste. The study was conducted in three stages. In the first stage, the solar ponds used for evaporating the effluent were converted into high rate algal ponds with *Chroococcus turgidus*, a blue green alga. Algal growth increased the pH and fresh untreated acidic effluent was introduced until the pH of the effluent was reduced to the desired level depending on the amount of effluent already in the tank. When allowed to stand, the pH of the effluent increased from 6.0 to 8.2 in 4 days. In stage 2, pilot plant studies were undertaken in a sloping tank to reduce the time taken for the pH to increase. The pH increased within hours and enhanced evaporation also occurred. The sludge formation was negligible. In the final stage, based on the results of pilot plant studies, a full scaling up of the slope tank was made. With the addition of around 30 kl of acidic effluent every day, the pH of the effluent remained constant around 7.02 and total dissolved salts stabilized at 49 g/l. There was no sludge formation even after 2 years of operation. With just one circulation of the effluent at a pumping rate of 80 kl/h on the slopes, the desired evaporation of 30 kl was achieved.

**KEYWORDS:** *Chroococcus turgidus*, effluent treatment, pH correction, algal biomass

## INTRODUCTION

Phycoremediation, as defined by Olguín<sup>1</sup> in a broad sense, is the use of macroalgae or microalgae for the removal or biotransformation of pollutants, including nutrients and xenobiotics from wastewater and CO<sub>2</sub> from waste air. Microalgae play an important role during the treatment of domestic wastewater<sup>2–6</sup>. Recent studies have shown that microalgae can support the aerobic degradation of various hazardous contaminants<sup>7–9</sup>. Microalgae can efficiently remove nutrients and can degrade and remove a wide range of inorganic and organic pollutants<sup>10–13</sup>. Microalgal species have been successfully used for the treatment of olive oil mill wastewater and paper industry wastewater<sup>14,15</sup>. Lima et al<sup>16</sup> reported *p*-nitrophenol removal by a consortium of microalgae. Microalgae could be also used to degrade azo dyes<sup>17</sup>.

### Phycoremediation of industrial effluents

Industrial effluents are conventionally treated using a variety of hazardous chemicals for pH correction, sludge removal, colour removal, and odour removal. Extensive use of chemicals for effluent treatment re-

sults in a huge amount of sludge which forms the so-called hazardous solid waste generated by the industry and which must be disposed by depositing it in landfills. Algal technology avoids the use of chemicals and the whole process of effluent treatment is simplified. There is considerable reduction in sludge formation. Algal technology is very economical and safe for the environment<sup>18–21</sup>.

The present study was done on the phycoremediation of effluent from SNAP Alginate and Natural Products Ltd. situated at Ranipet, Tamil Nadu, India. SNAP is involved in the production of alginate of various grades from *Sargassum* sp. Their liquid effluent (generated at 30 kl per day) is highly acidic (around pH 1.4–1.8) due to the use of sulphuric acid as their process material. The Pollution Control Board regulations require that the acidic effluent is neutralized, and the industry was using caustic for that purpose. The solar ponds used for evaporating the effluent were converted to high rate algal (HRA) ponds and a pilot slope tank study was undertaken to shorten the duration of the pH increase, which was later scaled up.

Preliminary laboratory experiments revealed that

*Chroococcus turgidus*, a cyanophycean microalga, has the potential to increase pH and decrease total dissolved solids (TDS) and has a wide tolerance to pH and high salinity<sup>22-24</sup>.

## MATERIALS AND METHODS

SNAP manufacture alginic acid and its various salts from the brown algae *Sargassum* and *Turbinaria* which are procured from the Gulf of Mannar, South India. In the industry, seaweeds are treated with mild acid for removal of unwanted salts and then treated with alkali for conversion of alginic acid into sodium alginate. The digested pulp is then diluted and settled and sodium alginate is recovered.

SNAP generates a solid and a liquid discharge. The solid discharge consists of the remains of seaweeds after the extraction of alginates which are composted. The liquid discharge is the wash water of the seaweeds, which is acidic and essentially contains organic TDS, sea salts, and sea sand.

The spent water generated was divided in to three main categories: neutral, alkaline, and acid streams. The neutral water stream consists of wash water of various process equipments, tanks and floor, and the condensate water from the boiler. The alkaline water stream is produced during the digestion. The seaweeds are digested under alkaline conditions. The digested seaweeds are diluted with water and settled to remove the seaweed residue. The supernatant liquid from the settler is taken for further processing. The seaweed residue is further washed thoroughly and dewatered. The collected water is taken in the 'alkali water recycle' tank and reused for diluting the digested seaweeds. As for the acid water stream, the supernatant liquid from the settling tanks is acidified and precipitated to recover the product. The acidic water is collected in the acidic water recycle tank. A portion of the acidic water is neutralized and taken with the alkali recycle water and reused for diluting the digested seaweeds. A portion of the acidic water is reused for washing the seaweeds. About 30 kl of acidic water as a blow down is sent to the treatment plant.

The acidic water was neutralized with caustic soda by the industry, settled to remove the total suspended solids and evaporated on solar evaporation ponds (SEPs). The dried solids were recovered from the SEP and stored in a secured landfill.

Improvised CFTRI Medium<sup>25</sup>, Bold Basal Medium<sup>26</sup> and F/2 medium<sup>27</sup> were prepared for laboratory cultivation of microalga.

## Microalga

*C. turgidus* was isolated from SNAP ETP site and identified following the monograph of Desikachary<sup>28</sup>. As *Chroococcus* sp. can grow in both fresh water and salt media, it was first inoculated in Bold Basal medium and was then transferred to F/2 medium for maintenance. Laboratory cultivation was carried out at  $24 \pm 1$  °C in a thermostatically controlled room and illuminated with cool white fluorescent lamps (Philips 40 W, cool daylight 6500k) at an intensity of 2000 lux in a 12:12 light dark regime. All the physical and chemical parameters were analysed according to APHA Standard Methods<sup>29</sup>.

## Ponds

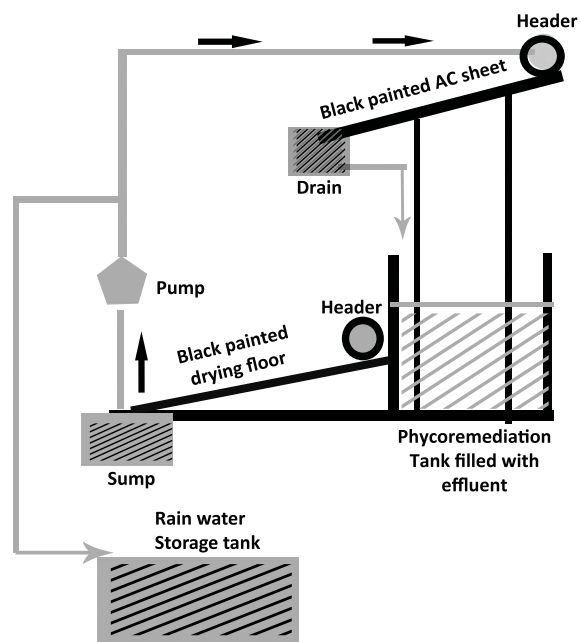
The SEPs were built to evaporate the liquid effluent after neutralization. The total area covered was 11 000 m<sup>2</sup>. The number of ponds built was 11. All the ponds were built in concrete and had a depth of 45 cm. Each pond is interconnected in such a way that the flow of effluent is by gradient. 30 kl of effluent is the input per day. To evaporate 30 kl of water per day at 4.5 mm per day the required area of the pond is 6750 m<sup>2</sup>. For our experimental purposes, Tank A (40 m × 47.5 m × 45 cm) was used. The area covered was 1900 m<sup>2</sup> and the total capacity was 8850 l. The depth of the effluent was maintained below 40 cm. The SEPs were later termed HRA ponds when phycoremediation was employed. No mixing, agitation, or aeration was done.

## Sloping pond - pilot scale

The pilot scale sloping pond was constructed in reinforced cement concrete (RCC) and was designed with a dimension of 2 m (L) × 2 m (W) × 0.75 m (depth) with a sloping angle of the evaporating surface of 45°. The dimension of the sloping area was 4 m<sup>2</sup>. The holding capacity of the tank was 3000 l. The flow rate of the effluent was at 1800 l/h. 1 cm of water in the tank is equal to 40 l. The plant was run during the day for about 9.5 h.

## Sloping pond - scaled up

The scaled-up sloping pond was constructed in RCC having a cross-sectional area of 1200 m<sup>2</sup> (70 m × 17.15 m parallelogram). The depth of the tank was 1 m and had a holding capacity of 1200 kl (Fig. 1). Pillars erected from the tank support the asbestos sheet sloped roof, angled at 45°. The slope angles from 240 cm to 165 cm for 23 m. This did not allow the rainwater to seep into the tank. The asbestos sheet was painted with black bitumen to improve the absorption of solar radiation.



**Fig. 1** Schematic diagram of phycoremediation sloping scaled-up plant.

At the ground level (bottom surface of the tank) a sloped floor area adjacent to the sloping tank was built. This was also painted with black bitumen. The slope was 15 cm and had an area of 3000 m<sup>2</sup> (70 m × 43 m). The effluent enriched with the alga was allowed to flow by gravity from the sloping pond tank. At the highest point of the sloping pond the effluent was pumped and from the roof it flowed down and collected in the sloping pond tank again. The effluent was pumped with the help of a 7.5 hp motor, which consumed around 40 to 45 units of electricity per day (Fig. 1).

The tank was of RCC with side walls measuring 70 m (W) × 21 m (L) × 1 m (D) with a thickness of 0.23 m. 120 concrete columns with a diameter of 22 cm were built in the tank of which 35 columns were on the sidewalls and the remaining 85 were in 5 rows of 17 each. The asbestos sheet was fastened to the columns with steel girders. The phycoremediation sloping tank faced in the east-west direction to maximize sun tracking. The tank had a capacity of 1200 m<sup>3</sup> with a sloped area (roof) of 1200 m<sup>2</sup> and a sloped floor area of 3000 m<sup>2</sup>. The total sloped area for evaporation was 4000 m<sup>2</sup>. The pump had a flow rate of 80 kl/h. On average 840 kl of effluent was maintained in the tank.

Test bore wells of 22 cm diameter and 300 cm depth, three each on both sides of the phycoremedi-

**Table 1** A comparison of physic-chemical parameters of raw effluent with effluent taken from the bottom of the tank after 2 years of phycoremediation (evaporation at 30 kl/day/2 years) (values ± SD).

Parameters	Raw effluent	After 2 years
Turbidity NTU	106 ± 7.20	5.9 ± 0.15
TDS (mg/l)	27 600 ± 600	49 220 ± 230
Conductivity (µmhos/cm)	36 430 ± 120	69 896 ± 354
pH	1.66 ± 0.15	7.02 ± 0.17
Alkalinity Ph (mg/l)	0	0
Alkalinity (mg/l)	-	2916 ± 160.8
Total hardness (mg/l)	2100 ± 123	5125 ± 110
Ca (mg/l)	520 ± 15.7	1120 ± 49.3
Mg (mg/l)	192 ± 4.2	558 ± 7.7
Na (mg/l)	6800 ± 143.7	7750 ± 123.5
K (mg/l)	700 ± 15.3	8125 ± 150.7
Fe (mg/l)	17.99 ± 0.34	4.13 ± 0.19
Mn (mg/l)	-	-
Free ammonia (mg/l)	56 ± 7.2	13.44 ± 0.28
NO <sub>2</sub> (mg/l)	0.43 ± 0.04	-
NO <sub>3</sub> (mg/l)	22 ± 1.5	16 ± 1.2
Chloride (mg/l)	3216 ± 14.6	12 189 ± 110
Fluoride (mg/l)	0.62 ± 0.14	0
Sulphate (mg/l)	5221 ± 110.8	1195 ± 89.3
Phosphate (mg/l)	28.62 ± 1.22	169 ± 5.67
SiO <sub>2</sub> (mg/l)	5.48 ± 0.23	79.49 ± 3.45
BOD (mg/l)	44 ± 5.6	960 ± 23.5
COD (mg/l)	148 ± 12.5	3266 ± 24.6

ation sloping tank, were built to detect any seepage of effluent. The bore wells were periodically tested for any difference in TDS, chemical oxygen demand (COD), biological oxygen demand (BOD), and pH.

## RESULTS AND DISCUSSION

### Effluent analysis and conventional treatment in SEPs

The raw effluent was analysed for its physico-chemical parameters and the results are shown in Table 1. The amount of TDS was quite high (27 600 mg/l). As sulphuric acid and sodium carbonate were used in the process, the levels of sodium and sulphate were high (6800 mg/l and 5221 mg/l, respectively). Chlorides were also high (3216 mg/l). The conventional treatment method of neutralizing the acidic effluent with NaOH was followed and the effluent was allowed to evaporate in solar ponds.

### Modified treatment in SEPs using *C. turgidus*

All the 11 solar ponds were interconnected in such a way that the flow of effluent was by gradient. By adjusting the initial pH to 6.5 *C. turgidus* was encouraged to grow in the raw effluent. As the pH

**Table 2** Maintenance of pH in solar ponds (Tank A).

Day <sup>a</sup>	Quantity of effluent (l)	Input of effluent (l)	pH ( $\pm$ SD)	Evaporation (l)
1	51 600		7.79 $\pm$ 0.11	
2	44 100	30 000	6.93 $\pm$ 0.16	7500
3	66 500		6.96 $\pm$ 0.18	7600
4	58 900		7.36 $\pm$ 0.2	7600
5	51 300		7.46 $\pm$ 0.14	7600
6	43 800		7.66 $\pm$ 0.20	7500
7	36 100		7.85 $\pm$ 0.24	7700
8	28 500	30 000	6.97 $\pm$ 0.35	7600
9	51 000		7.41 $\pm$ 0.50	7500
10	43 500		7.62 $\pm$ 0.43	7500

<sup>a</sup> Experiments carried out in February – all days sunny, max temp = 33 °C. All readings taken at the end of the day.

rose, fresh untreated acidic effluent was introduced until the pH of the effluent was reduced to the desired level depending on the amount of effluent already in the tank. Care was taken so as not to bring down the pH to less than 6.5. The effluent was treated according to the procedure in Table 2.

When allowed to stand, the pH of the effluent increased from 6.5 to 8.2 in 4 days with a sunlight intensity of around 55 to 60 klux. The average maximum temperature was 35 °C. It may be noted that the colour of the raw effluent was pale brown. As the pH increased, it turned greenish brown, then yellowish brown, and finally pink. When fresh acidic raw effluent was added to the standing effluent with a high pH, the colour of the effluent changed according to the pH as mentioned above. The algal cell density reached  $2300 \times 10^4$  cells/ml.

Daily salt input in the effluent was 2.7 g/l. With an average 30 kl of effluent per day, the salt input was 800 kg per day (or 290 tons/year). But when dried completely after a year the total solids were only 34.8 tons. That is to say only 12% of the expected total solids were found. There was 88% reduction in TDS.

### Sloping pond - pilot studies

With the HRA pond, the desired pH increase occurred in 4–6 days. If the algal growth could be enhanced by better aeration and mixing, the time taken to increase the pH could be reduced. Aeration and agitation can improve the growth of algae and this could be achieved by circulating the effluent in a sloping pond. This could also increase the rate of evaporation. Hence it was decided to try sloping pond technology. Pilot plant sloping pond studies were undertaken.

The principle of the sloping design is to create a turbulent flow while the algal suspension flows through sloping surfaces. A pump returns the algal suspension from the lowest point to the top. The turbulence is produced by gravity. The flow speed of the liquid increases with the slope of the surface. Effluent enriched with *C. turgidus* was loaded into the slope pilot tank.

### Trials with varying sloping surfaces

We first tried using a sloping surface made from galvanized iron (GI) sheet. The sheet was painted black so as to absorb as much heat as possible. The pH of the effluent was maintained in spite of adding 60 l of acidic effluent intermittently (Table 3). Evaporation was also significant at 40 l per day with the maximum temperature being 32 °C. But the problem encountered with GI sheets was erosion and corrosion. The tip of the slope corroded and cracks in the paint occurred within a month. Hence we instead decided to use asbestos sheet coated with bitumen. A similar increase in pH and evaporation was achieved (Table 3). There was no corrosion and the bitumen also was stable. The temperature was measured between the white surface and the black surface of the sheet. A sloping surface of concrete coated with bitumen was also tried. The pH was stable and the evaporation was at 40 l per day (Table 3).

Further studies were done to observe the change in pH and evaporation by increasing the number of circulations (by increasing the flow rate). The number of circulation was increased from 7 to 33 per day and, as a result, the evaporation increased from 20 l to 48 l per day. The pH of the effluent was stable in spite of addition of 60 l of acidic effluent. The number of circulations of the effluent enriched with *C. turgidus* did not have any effect on the pH (Table 4). The effluent remained green and the cell density of *C. turgidus* remained constant and was around  $3600 \times 10^4$  cells per ml.

### Phycoremediation sloping pond - scaled up

After the successful completion of the pilot plant studies, it was decided to scale up the plant to 1000 times the capacity of the pilot plant. The pilot plant had a sloping area of 4 m<sup>2</sup>. It was decided to have a sloping area of 4000 m<sup>2</sup> in two stages, one on the roof and the other on the floor (Fig. 1). With a holding capacity 1200 kl it can accommodate 40 days of effluent generation at 30 kl a day.

The plant was initiated with 720 l of effluent from a SEP, which was already enriched with *C. turgidus*. The effluent had an initial pH of 6.85. From day

**Table 3** Pilot plant studies with various slope surfaces (pH values  $\pm$  SD).

Slope surface	Initial dip (cm) <sup>a</sup>	Final dip (cm) <sup>a</sup>	Makeup Effluent pH	Initial pH	Final pH	Evap (cm) <sup>a</sup>	T <sub>max</sub> slope surface (°C)	T <sub>max</sub> in tank (°C)	T <sub>max</sub> room (°C)	Max RH (%)
Cement slab	41	40.5	1.65 $\pm$ 0.03	7.12 $\pm$ 0.15	7.86 $\pm$ 0.05	0.50	33	32	32.5	56
	42	41	1.72 $\pm$ 0.05	7.26 $\pm$ 0.02	7.99 $\pm$ 0.07	1.00	36	34	34	53
	43	42	1.69 $\pm$ 0.01	7.52 $\pm$ 0.05	8.12 $\pm$ 0.06	1.00	33	30.5	32	54
	43.5	42.5	1.72 $\pm$ 0.11	7.14 $\pm$ 0.03	7.88 $\pm$ 0.10	1.00	34.5	33	34	58
	43	42	1.69 $\pm$ 0.23	7.08 $\pm$ 0.07	7.88 $\pm$ 0.03	1.00	34.5	33	35	59
Asbestos sheet	43	42	1.62 $\pm$ 0.11	7.22 $\pm$ 0.03	7.97 $\pm$ 0.12	1.00	36	34	35	59
	30.5	29.5	1.71 $\pm$ 0.05	7.62 $\pm$ 0.13	8.12 $\pm$ 0.14	1.00	41.5	37.5	35	55
	31	30	1.69 $\pm$ 0.12	7.69 $\pm$ 0.34	8.17 $\pm$ 0.13	1.00	42	38	36	56
	32	31	1.72 $\pm$ 0.11	7.65 $\pm$ 0.04	8.12 $\pm$ 0.07	1.00	42	38.5	36.5	57
	32.5	31.5	1.69 $\pm$ 0.02	7.66 $\pm$ 0.01	8.22 $\pm$ 0.08	1.00	42	38	36.5	54
GI sheet	33	32	1.72 $\pm$ 0.09	7.69 $\pm$ 0.23	8.26 $\pm$ 0.34	1.00	39.5	37	35	55
	32.5	31.5	1.72 $\pm$ 0.08	7.79 $\pm$ 0.03	8.28 $\pm$ 0.12	1.00	41.5	38	36	55
	17	16.5	1.71 $\pm$ 0.1	6.69 $\pm$ 0.01	7.12 $\pm$ 0.18	0.50	35	31	30.5	52
	18	17.5	1.69 $\pm$ 0.13	4.85 $\pm$ 0.16	5.72 $\pm$ 0.03	0.50	35	31	31	53
	18.2	17.2	1.79 $\pm$ 0.04	5.46 $\pm$ 0.7	6.24 $\pm$ 0.54	1.00	36	32	31	52
	17.7	16.7	1.72 $\pm$ 0.12	5.24 $\pm$ 0.19	6.12 $\pm$ 0.11	1.00	36	32	31.5	54
	17.5	16.5	1.75 $\pm$ 0.35	5.25 $\pm$ 0.10	6.54 $\pm$ 0.22	1.00	35	31	31	52
17	16	1.62 $\pm$ 0.11	6.7 $\pm$ 0.24	7.06 $\pm$ 0.17	1.00	36	31.5	31.5	53	

Evap = evaporation; RH = relative humidity

Circulation pump started at 8.30 am and stopped at 6.00 pm every day. Flow rate of 0.5 s<sup>-1</sup> was maintained. Sunny throughout the experiment.

<sup>a</sup> 1 cm = 40 l

**Table 4** Effect on pH and evaporation due to increase in circulation (pH values  $\pm$  SD).

S No.	Initial Dip (cm) <sup>a</sup>	Final Dip (cm) <sup>a</sup>	Makeup Effluent pH	Initial pH	Final pH	Evap (l)	No. of circulation	T <sub>max</sub> slope surface (°C)	T <sub>max</sub> in tank (°C)	T <sub>max</sub> room (°C)	Max RH (%)
1	22.1	21.3	1.69 $\pm$ 0.12	8.34 $\pm$ 0.09	8.24 $\pm$ 0.07	48	33	33	30.5	32	56
2	14.5	13.5	1.65 $\pm$ 0.06	7.61 $\pm$ 0.11	7.52 $\pm$ 0.06	40	24	34.5	33	34	53
3	9.5	8.9	1.78 $\pm$ 0.12	7.42 $\pm$ 0.14	7.63 $\pm$ 0.16	24	10	34.5	33	35	54
4	43.5	43	1.75 $\pm$ 0.09	8.11 $\pm$ 0.08	7.92 $\pm$ 0.13	20	7	36	34	35	58

Slope - Cement Slab

Circulation pump started at 8.30 am and stopped at 6.00 pm every day. Addition of effluent at 60 l/day. Sunny throughout the experiment.

<sup>a</sup> 1 cm = 40 l

1 onwards, the pH stabilized around 7 and the TDS was around 45 000 mg/l. The average load of effluent was around 850 l and just one circulation was enough to evaporate 25 to 30 kl of effluent. Even at the end of 9 months, the data remained the same (Table 5). The effluent remained green and the count of *Chroococcus* remained constant and was around 4500  $\times$  10<sup>4</sup> cells/ml. During rainy days the plant also served as a good rainwater-harvesting unit. Whenever there was rain, phycoremediation was stopped and the rainwater collected was sent to a water storage tank.

Conventionally NaOH is used to neutralize acidic effluents. Chemical neutralization costs could be reduced significantly with an integrated iron oxidation and limestone neutralization process because limestone is less expensive than lime, and a high-solids-content sludge is produced<sup>30</sup>. Benassi et al<sup>31</sup> suggested that chitosan microspheres could be used as an alternative approach for remediation of acidic coal mining wastewaters.

Anaerobic conversion of an acidic petrochemical

**Table 5** pH and evaporation studies in scaled-up phycoremediation plant.

Day	Dip (cm) <sup>a</sup>	pH $\pm$ SD	Evap (kl)	TDS $\pm$ SD (mg/l)
1	76.5	7.09 $\pm$ 0.34		47 640 $\pm$ 234.3
2	77	6.9 $\pm$ 0.43	25.4	44 310 $\pm$ 256.0
3	76.5	7.3 $\pm$ 0.55	26.6	46 820 $\pm$ 245.7
4	76	6.8 $\pm$ 0.67	27.8	47 360 $\pm$ 289.0
5	76	6.8 $\pm$ 0.12	26.0	46 930 $\pm$ 210.4
6	74.5	6.74 $\pm$ 0.23	29.0	48 300 $\pm$ 289.0
7	74.5	6.85 $\pm$ 0.36	26.0	47 820 $\pm$ 256.8

Study at the end of 9 months of operation

Input effluent = 26 kl.

<sup>a</sup> 1 cm = 1200 l

effluent into a methane-rich biogas was achieved using an up flow anaerobic sludge blanket reactor<sup>32</sup>. The natural evolution of acidic waters, (which includes the bacterial oxidation of Fe (II) and the subsequent precipitation of Fe (III) minerals), representing an efficient mechanism of attenuation was reported by

Javier Sánchez et al<sup>33</sup>. Costa and Duarte<sup>34</sup> showed the possibility of bioremediation of acid mine drainage using acidic soil and organic wastes for promoting sulphate-reducing bacterial activity on a column reactor. Jayachandran et al<sup>35</sup> using *Acinetobacter* sp could reduce the COD content in the acidic effluent effectively. COD values could further be reduced in an acidic petrochemical effluent by influencing the anaerobic digestion by different substrate pH values<sup>36</sup>.

Utilizing the alkalinity produced by the alga *Spirulina*, precipitating heavy metals in acid mine drainage has been demonstrated by Van Hille et al<sup>37</sup>. The ability of certain algal species to increase the alkalinity of the surrounding medium as a byproduct of their inorganic carbon accumulation mechanism has been documented<sup>38</sup>.

#### Phycoremediation using sloping tank - scaled up

Encouraged by the pilot plant studies, a fully scaled up sloping phycoremediation plant was commissioned in September 2006. With the addition of around 30 kl of acidic effluent every day, the pH of the effluent remained constant at around 7.0 and the TDS stabilized at 49 000 mg/l. There was no sludge formation even at the end of two years of operation (Table 1). Even after just one circulation of the effluent with a pumping rate of 80 kl per hour on the slopes, the desired evaporation of 30 kl was achieved. The level in the tank was kept around 850 kl against the tank capacity of 1200 kl. The sloping tank also served as a rainwater-harvesting unit during rainy days. It has been estimated that the amount of rainwater that could be harvested during a normal rainy season can supply 6 months water requirement for this industry. Presence of another blue-green alga, *Oscillatoria* only on the slopes of the sloping pond added to the efficiency of phycoremediation. The removal of *Oscillatoria*, which formed a thick scum over the sloping evaporating surface at the ground level, drastically reduced evaporation by 50%.

Bioremediation removes the toxic pollutants once and for all. The pollutants may be bio-converted, biodegraded, or volatilized. Neumann et al<sup>39</sup>, established the fact that even metals like selenium are converted to volatile dimethylselenide by microalgae. Photoevaporation of bio-molecules by higher plants has been demonstrated with mass balance studies<sup>40</sup>. Luther<sup>10</sup> has reported that the alga *Scenedesmus obliquus* was able to utilize naphthalenesulphonic acids as a source of sulphur for their biomass, releasing the carbon ring into the medium. Bio-utilization, bio-transformation, and bio-evaporation may explain the reason for TDS remaining stable at 49 000 mg/l even after the addition of 30 kl of effluent per day with

a TDS of 27 600 mg/l. Our preliminary laboratory studies also revealed that *C. turgidus* reduced the levels of potassium, sodium, iron, chlorides, fluorides, sulphates and TDS to a large extent<sup>22-24</sup>. So far, almost all the bioremediation technologies in treating acidic waters have been limited to the laboratory scale.

#### CONCLUSIONS

The first ever phycoremediation plant with *C. turgidus* has been working from September 2006 at SNAP industry very successfully. The plant evaporates 30 kl effluent every day without developing any sludge. pH correction and sludge reduction could be achieved without employing any chemicals. The industry is saving a substantial amount of money on chemicals and the environment is spared from the dumping of hazardous solid waste. We expect that phycoremediation technology could be employed to deal with other types of industrial effluents with similar success.

**Acknowledgements:** The authors thank the Chairman of the Vivekananda Institute of Algal Technology, Chennai for facilities and M/S SNAP Natural and Alginate Products, Ranipet for the research grant.

#### REFERENCES

1. Olguín EJ (2003) Phycoremediation: key issues for cost-effective nutrient removal process. *Biotechnol Adv* **22**, 1–91.
2. Aziz MA, Ng WJ (1993) Industrial wastewater treatment using an activated algae-reactor. *Water Sci Tech* **28**, 71–6.
3. Abeliovich A (1986) Algae in wastewater oxidation ponds. In: Richmond A (ed) *Handbook of Micro-algal Mass Culture*, CRC Press, Boca Raton, pp 331–8.
4. Mara DD, Pearson H (1986) Artificial freshwater environment: waste stabilization ponds. In: Rehm HJ, Reed G (eds) *Biotechnology*, Verlagsgesellschaft, pp 177–206.
5. Oswald WJ (1988) Micro-algae and waste-water treatment. In: Borowitzka MBL (ed) *Micro-algal Biotechnology*, Cambridge Univ Press, pp 305–28.
6. Oswald WJ (1995) Ponds in the twenty-first century. *Water Sci Tech* **31**, 1–8.
7. Muñoz R, Köllner C, Guieysse B, Mattiasson B (2004) Photosynthetically oxygenated salicylate biodegradation in a continuous stirred tank photobioreactor. *Biotechnol Bioeng* **87**, 797–803.
8. Muñoz R, Jacinto MSA, Guieysse B, Mattiasson B (2005) Combined carbon and nitrogen removal from acetonitrile using algal-bacterial reactors. *Appl Microbiol Biotechnol* **67**, 699–707.
9. Muñoz R, Rolvering C, Guieysse B, Mattiasson B (2005) Photosynthetically oxygenated acetonitrile

- biodegradation by an algal–bacterial microcosm: a pilot scale study. *Water Sci Tech* **51**, 261–5.
10. Luther M (1990) Degradation of different substituted aromatic compounds as nutrient sources by the green alga *Scenedesmus obliquus*. Dechema Biotechnol Conf, vol 4, pp 613–5.
  11. Craggs RJ, Smith VJ, McAuley PJ (1995) Wastewater nutrient removal by marine microalgae cultured under ambient conditions in mini-ponds. *Water Sci Tech* **31**, 151–60.
  12. Garbisu C, Alkorta I, Llama MJ, Serra JL (2000) Immobilization of living microalgae and their use for inorganic nitrogen and phosphorous removal from water. In: Olguín EJ, Sánchez G, Hemández E (eds) *Environmental Biotechnology and Cleaner Bioprocesses*, Taylor & Francis, London, pp 107–21.
  13. Muthukumar M, Raghavan BG, Subramanian VV, Sivasubramanian V (2005) Bioremediation of industrial effluent using micro algae. *Indian Hydrobiol* **7**, (Suppl) 105–22.
  14. Yewalkar SN, Dhumal KN, Sainis JK (2007) Chromium(VI)-reducing *Chlorella* spp. isolated from disposal sites of paper-pulp and electroplating industry. *J Appl Phycol* **19**, 459–65.
  15. Sánchez S, Martínez ME, Espejo MT, Pacheco R, Espinola F, Hodaifa G (2001) Mixotrophic culture of *Chlorella pyrenoidosa* with olive-mill wastewater as the nutrient medium. *J Appl Phycol* **13**, 443–9.
  16. Lima SAC, Castro PML, Morais R (2003) Biodegradation of *p*-nitrophenol by microalgae. *J Appl Phycol* **15**, 137–42.
  17. Jinqi I, Houtian O (1992) Degradation of azo dyes by algae. *Environ Pollut* **75**, 273–8.
  18. Kamaleswari J, Murugesan S, Sivasubramanian V (2007) Screening of freshwater algae for phycoremediation potentialities of industrial effluents and wastewater. *Ecol Environ Conservation* **13**, 697–701.
  19. Kamaleswari J (2008) Screening of freshwater algae for phycoremediation potentialities of industrial effluents and wastewater. PhD thesis, Univ of Madras.
  20. Ranjithkumar R (2008) Phycoremediation of acidic industrial effluents. PhD thesis, Univ of Madras.
  21. Hanumantharao P (2008) Phycoremediation of effluent from a leather processing chemical industry. PhD thesis, Univ of Madras.
  22. Ranjithkumar R (2004) Studies on the extraction and purification of pigments from the effluent of an alginate industry. MPhil thesis, Univ of Madras.
  23. Natarajan K (2004) Studies on the biotechnological potentials of *Chroococcus* sp isolated from industrial effluent. MPhil thesis, Univ of Madras.
  24. Varutharajan P (2005) Bioremediation of industrial effluent using micro algae. MPhil thesis, Univ of Madras.
  25. Venkataraman LV, Becker EW (1985) *Biotechnology and utilization of Algae, The Indian Experience*. Dept of Science and Technology, New Delhi, India.
  26. Nichols HW, Bold HC (1965) *Growth media – Fresh water*. In: Stein JR (ed) *Handbook of Physiological Methods*, Cambridge Univ Press pp 7–24.
  27. Guillard RR Land Ryther JH (1962) Studies on marine planktonic diatoms. I. *Cyclotella nana* Hustedt and *Detonula confervacea* (Cleve Grun). *Can J Microbiol* **8**, 229–39.
  28. Desikachary TV (1959) *Cyanophyta*, ICAR, New Delhi.
  29. American Public Health Association (2000) *Standard Methods for Examination of Water and Waste Water*, 21st edn, APHA, Washington DC.
  30. Maree JP, de Beer M, Strydom WF, Christie ADM, Waanders FB (2004) Neutralizing coal mine effluent with limestone to decrease metals and sulphate concentrations. *Mine Water Environ* **23**, 81–6.
  31. Benassi JC, Laus R, Geremias R, Lima PL, Menezes CTB, Laranjeira MCM, Wilhelm-Filho D, Fávère VT, Pedrosa RC (2006) Remediation of evaluation of coal mining wastewater by using chitosan microspheres biomarkers. *Arch Environ Contam Toxicol* **51**, 633–40.
  32. Nel LH, De Haast J, Britz TJ (1984) Anaerobic digestion of a petrochemical effluent using an upflow anaerobic sludge blanket reactor. *Biotechnol Lett* **6**, 741–6.
  33. Sánchez J, López E, Santofimia E, Reyes J, Martín JA (2005) The natural attenuation of two acidic effluents in Tharsis and La Zarza-Perrunal mines (Iberian Pyrite Belt, Huelva, Spain). *Environ Geol* **49**, 253–66.
  34. Costa MC, Duarte JC (2005) Bioremediation of acid mine drainage using acidic soil and organic wastes for promoting sulphate-reducing bacteria activity on a column reactor. *Water Air Soil Pollut* **165**, 325–45.
  35. Jayachandran K, Suresh PV, Chandrasekaran M (1994) A novel Acinetobacter sp. for treating highly acidic rubber latex centrifugation effluent. *Biotechnol Lett* **16**, 649–54.
  36. Nel LH, Britz TJ (1986) The influence of different substrate pH values on the performance of a downflow anaerobic fixed bed reactor treating a petrochemical effluent. *Biotechnol Lett* **8**, 293–8.
  37. Van Hille RP, Boshoff GA, Rose PD, Duncan JR (1999) A continuous process for the biological treatment of heavy metal contaminated acid mine water. *Resour Conservat Recycl* **27**, 157–67.
  38. Shiraiwa Y, Goyal A, Tolbert NE (1993) Alkalinization of the medium by unicellular green algae during uptake of dissolved inorganic carbon. *Plant Cell Physiol* **34**, 649–57.
  39. Neumann PM, De Souza MP, Pickering IJ, Terry N (2003) Rapid microalgal metabolism of selenate to volatile dimethylselenide. *Plant Cell Environ* **26**, 897–905.
  40. Ramaswami A, Milford JB, Small MJ (2005) *Integrated Environmental Modeling: Pollutant Transport, Fate, and Risk in the Environment*, Wiley, New York.