

## Algal technology for effective reduction of total hardness in wastewater and industrial effluents

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### Abstract

Algae based remediation technology can provide an excellent solution for pollution problems. The present paper deals with application of algal technology (Phycoremediation) to reduce total hardness in waste waters and industrial effluents. Water samples from a few selected lakes and ponds of Kancheepuram district, Tamilnadu and industrial effluent samples from a soft drink manufacturing industry at Ahmedabad, textile dyeing industries from Tamilnadu and Ahmedabad were employed in the present investigation. Micro algal cultures obtained from VIAT culture collection were inoculated into the effluent samples both at laboratory scale and pilot scale level. A significant reduction in total hardness was observed in all the water samples. From the results obtained with both natural waters and industrial effluents it is evident that phycoremediation technology can effectively handle hardness and make the water reusable and industrial effluents become more suitable for R/O recycling.

### Introduction

Hard water has high concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions. Hardness is reported in terms of calcium carbonate and in units of milligrams per litre (mg/L). Hard water is generally not harmful to one's health but can pose serious problems in industrial settings, where water hardness is monitored to avoid costly breakdowns in boilers, cooling towers, and other equipment that handles water. In domestic settings, the hardness of water is often indicated by the non-formation of suds when soap is agitated in the water sample. Hardness in water is defined as concentration of multivalent cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Hard water also forms deposits that clog plumbing. Calcium and magnesium carbonates tend to be deposited as off-white solids on the surfaces of pipes and the surfaces of heat exchangers.

The term hardness total hardness is used to describe the combination of calcium and magnesium hardness. However, hardness values are usually quoted in terms of  $\text{CaCO}_3$  because this is the most common cause of scaling. The standard classifications are given below (Droste, 1997):

- Hardness mg/L as  $\text{CaCO}_3$
- Moderate 60-120
- Hard 120-180
- Very hard more than 180

Water softeners operate on the ion exchange process (specifically a cation exchange process where ions are exchanged). The hardness minerals (positively charged Calcium and Magnesium ions) attach themselves to the

resin beads while sodium on the resin beads is released simultaneously into the water. Softened water is not recommended for watering plants, lawns, and gardens due to its elevated sodium content. Bioremediation can be a better alternative technology to avoid usage of chemicals.

Algae based remediation technology can provide an excellent solution for pollution problems. Vivekananda Institute of Algal technology (VIAT), Chennai, a pioneer in algae based technology to treat industrial effluents has implemented phycoremediation technology in a number of industries in India (Sivasubramanian, 2006; Kamaleswari *et al* 2007; Arti Narasimhan *et al* 2008; Sivasubramanian *et al* 2009; Hanumantha Rao *et al* 2010; Sivasubramanian *et al* 2010; 2011; Hanumantha Rao *et al* 2011; Kamaleswari and Sivasubramanian 2011).

The present paper deals with application of algal technology (Phycoremediation) to reduce total hardness in waste waters and industrial effluents.

### Materials and Methods

#### *Micro algae and Media*

Micro algae employed in the present investigation were obtained from Algal Culture Collection of Vivekananda Institute of Algal Technology (VIAT), Chennai. They were grown in Bold Basal medium (Nichols and Bold, 1965) and CFTRI medium (Venkataraman, 1985).

#### *Water samples:*

Water samples from a few selected lakes and ponds of Kancheepuram district, Tamilnadu and industrial effluent samples from a soft drink manufacturing industry at

Ahmedabad, textile dyeing industries from Tamilnadu and Ahmedabad were employed in the present investigation.

*Pilot tank for effluent treatment*

The pilot sloping pond was constructed in RCC and was designed with a dimension of 268 cm. (Length) x 238 cm. (Width) x 64 cm. (Depth) with a sloping angle (made of GI sheet) of the evaporating surface at 150. The dimension of the sloped area was 2.53 m<sup>2</sup>. The flow rate of the effluent was maintained at 59.6 L/day (litres per day). 1 cm of water in the tank equaled 63.7 L and the plant was run during the day for about 9 hrs.

Analysis of physic – chemical parameters was done following APHA Standard Methods ( APHA. 1985)

**Results and Discussion**

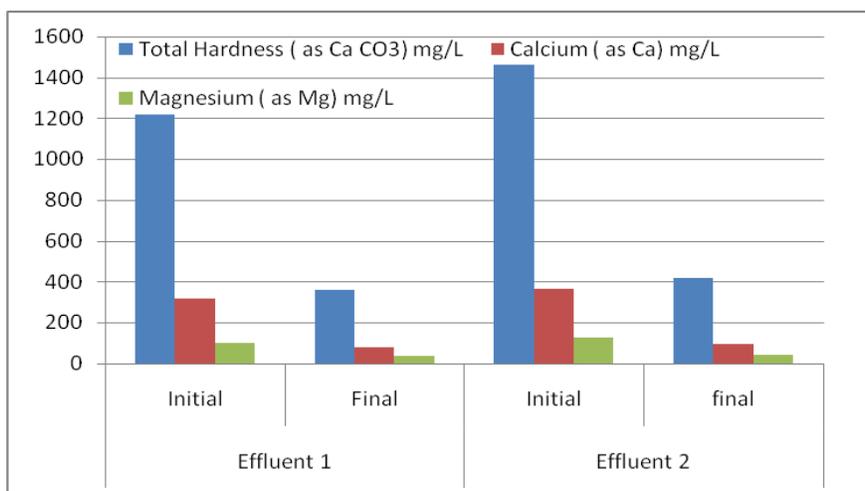
*Industrial effluents*

Water samples were inoculated with micro algae obtained from VIAT, Chennai. Analysis of total hardness was done after 7 days incubation. Table 1 and Fig 1 show results of laboratory level treatment of effluent samples (1 and 2) from a soft drink manufacturing industry, Ahmedabad by employing *Chlorococcum humicola*. Algal treatment has reduced total hardness to about 71 % in both the samples. Ca<sup>2+</sup> and Mg<sup>2+</sup> were also reduced significantly. Table 2 and Fig 2 show Table 1 and Fig 1 show results of laboratory level treatment of effluent samples (1 and 2) from a soft drink manufacturing industry, Ahmedabad by employing *Chlorella conglomerata*. There was 63 to 74% reduction in total hardness. Ca<sup>2+</sup> and Mg<sup>2+</sup> were also reduced effectively by *Chlorella sp.*

**Table 1** Effect of algal treatment on total hardness of effluent from soft drink manufacturing industry at Ahmedabad – Lab study using *Chlorococcum humicola*

| Parameters                                    | Effluent 1 |       |             | Effluent 2 |       |             |
|---|------------|-------|-------------|------------|-------|-------------|
|   | Initial    | Final | % reduction | Initial    | final | % reduction |
| Total Hardness ( as Ca CO <sub>3</sub> ) mg/L | 1220       | 360   | <b>70.5</b> | 1460       | 420   | <b>71.2</b> |
| Calcium ( as Ca) mg/L                         | 320        | 81    | <b>74.7</b> | 368        | 96    | <b>73.9</b> |
| Magnesium ( as Mg) mg/L                       | 101        | 36    | <b>64.4</b> | 129        | 43    | <b>66.6</b> |

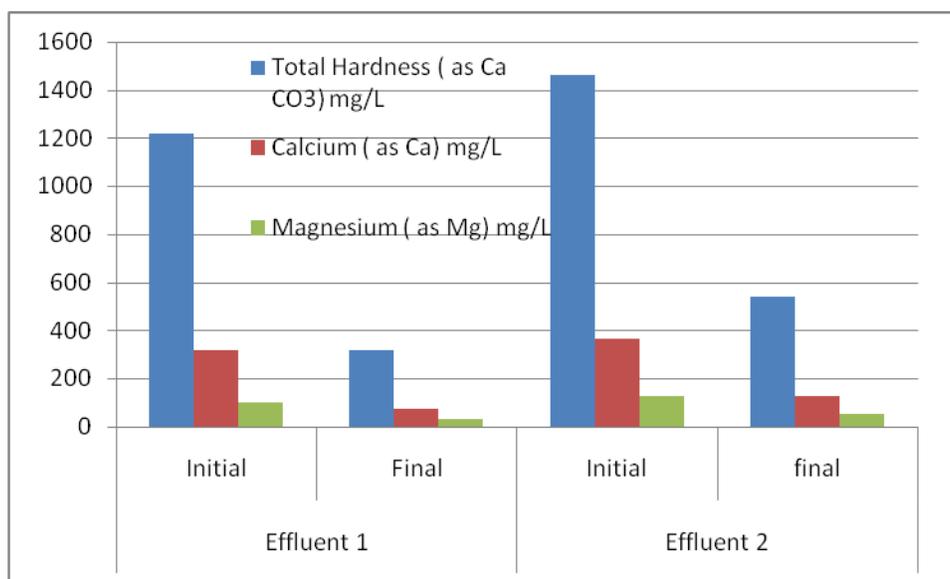
**Fig 1.** Effect of algal treatment on total hardness of effluent from soft drink manufacturing industry at Ahmedabad – Lab study using *Chlorococcum humicola*



**Table 2** Effect of algal treatment on total hardness of effluent from soft drink manufacturing industry at Ahmedabad – Lab study using *Chlorella conglomerata*

| Parameters                                    | Effluent 1 |       |             | Effluent 2 |       |             |
|---|------------|-------|-------------|------------|-------|-------------|
|   | Initial    | Final | % reduction | Initial    | final | % reduction |
| Total Hardness ( as Ca CO <sub>3</sub> ) mg/L | 1220       | 320   | 73.8        | 1460       | 540   | 63          |
| Calcium ( as Ca) mg/L                         | 320        | 72    | 77.5        | 368        | 128   | 65.2        |
| Magnesium ( as Mg) mg/L                       | 101        | 34    | 66.3        | 129        | 53    | 58.9        |

**Fig 2.** Effect of algal treatment on total hardness of effluent from soft drink manufacturing industry at Ahmedabad – Lab study using *Chlorella conglomerate*



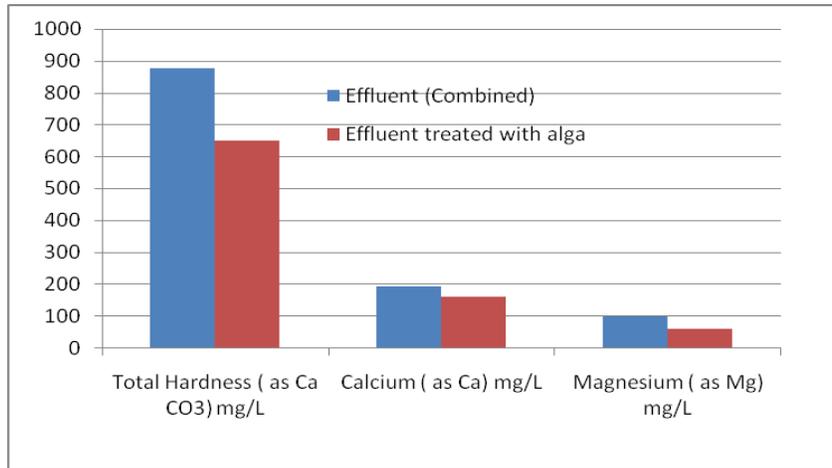
Textile dyeing effluent from an industry from Tamilnadu and Ahmedabad were treated with micro algae at laboratory level as well as pilot scale level in the industry itself. The results are given in Tables 3 to 7 and Fig 3 to 6. Combined effluent from textile dyeing industry from Tamilnadu when treated with algae at laboratory total hardness was reduced

to only 25%. But when the same effluent was treated with algae at pilot scale field level there was 87% reduction in total hardness. Similarly the dye bath effluent from this industry when treated at the field in pilot plant exhibited significant reduction in total hardness (84%).

**Table 3.** Effect of algal treatment on total hardness of combined effluent from textile dyeing industry at Tamilnadu – Lab study using *Chlorococcum humicola*

| Parameters                                    | Effluent (Combined) | Effluent treated with alga | % reduction |
|---|---------------------|----------------------------|-------------|
| Total Hardness ( as Ca CO <sub>3</sub> ) mg/L | 875                 | 650                        | 25.71       |
| Calcium ( as Ca) mg/L                         | 190                 | 160                        | 15.78       |
| Magnesium ( as Mg) mg/L                       | 96                  | 60                         | 37.5        |

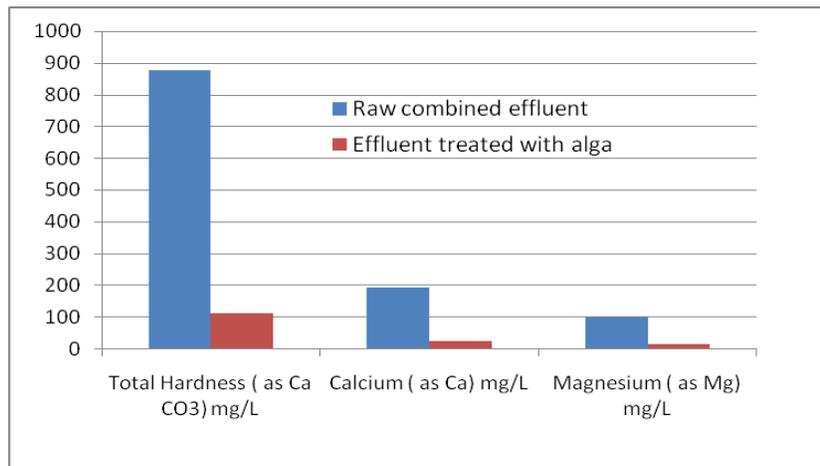
**Fig 3. Effect of algal treatment on total hardness of combined effluent from textile dyeing industry at Tamilnadu – Lab study using *Chlorococcum humicola***



**Table 4 Effect of algal treatment on total hardness of combined effluent from textile dyeing industry at Tamilnadu – Pilot field study using *Chlorococcum humicola***

| Parameters                                    | Raw combined effluent | Effluent treated with alga | % reduction  |
|---|-----------------------|----------------------------|--------------|
| Total Hardness ( as Ca CO <sub>3</sub> ) mg/L | 875                   | 110                        | <b>87.42</b> |
| Calcium ( as Ca) mg/L                         | 190                   | 24                         | <b>87.36</b> |
| Magnesium ( as Mg) mg/L                       | 96                    | 12                         | <b>87.5</b>  |

**Fig 4. Effect of algal treatment on total hardness of combined effluent from textile dyeing industry at Tamilnadu – Pilot field study using *Chlorococcum humicola***



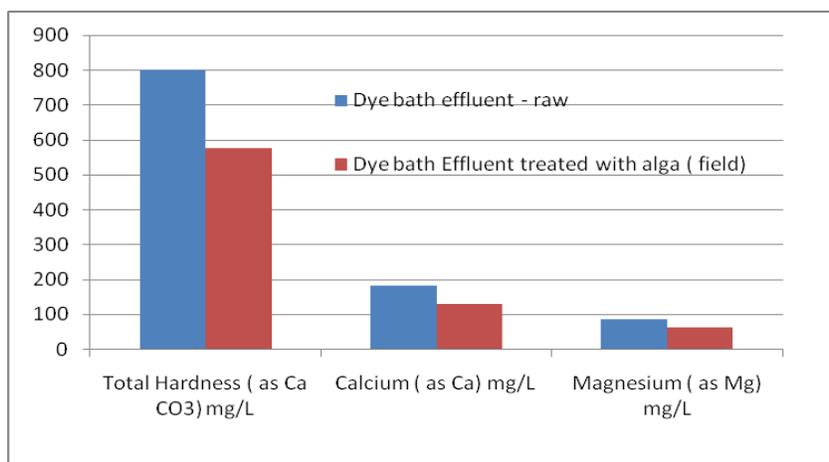
**Table 5. A comparison of laboratory treatment and field level pilot scale treatment on the reduction of hardness in combined effluent from textile dyeing industry at Tamilnadu**

| Parameters                                    | Raw combined effluent | Effluent treated with alga (lab) | Effluent treated with alga (field) | % Reduction (lab) | % Reduction (field) |
|---|-----------------------|----------------------------------|------------------------------------|-------------------|---------------------|
| Total Hardness ( as Ca CO <sub>3</sub> ) mg/L | 875                   | 650                              | 110                                | 25.71             | <b>87.42</b>        |
| Calcium ( as Ca) mg/L                         | 190                   | 160                              | 24                                 | 15.78             | <b>87.36</b>        |
| Magnesium ( as Mg) mg/L                       | 96                    | 60                               | 12                                 | 37.5              | <b>87.5</b>         |

**Table 6. Effect of algal treatment on total hardness of dye bath effluent from textile dyeing industry at Tamilnadu – Pilot scale study employing *Chlorococcum humicola*.**

| Parameters                                    | Dye bath effluent | Dye bath Effluent treated with alga ( field) | % reduction  |
|---|-------------------|--|--------------|
| Total Hardness ( as Ca CO <sub>3</sub> ) mg/L | 800               | 575  | <b>83.75</b> |
| Calcium ( as Ca) mg/L                         | 180               | 130  | <b>27.77</b> |
| Magnesium ( as Mg) mg/L                       | 84                | 60   | 30           |

**Fig 6 . Effect of algal treatment on total hardness of dye bath effluent from textile dyeing industry at Tamilnadu – Pilot scale study employing *Chlorococcum humicola*.**



**Table 7. A comparison of laboratory treatment and field level pilot scale treatment on the reduction of hardness in dye bath effluent from textile dyeing industry at Tamilnadu**

| Parameters                                    | Dye bath effluent | Dye bath Effluent treated with algae ( lab) | Dye bath Effluent treated with algae ( field) | % reduction in lab | % reduction from field |
|---|-------------------|---|---|--------------------|------------------------|
| Total Hardness ( as Ca CO <sub>3</sub> ) mg/L | 800               | 1325  | 575   | 0                  | <b>83.75</b>           |
| Calcium ( as Ca) mg/L                         | 180               | 290   | 130   | 0                  | <b>27.77</b>           |
| Magnesium ( as Mg) mg/L                       | 84                | 144   | 60  | 0                  | 30                     |

Water samples collected from selected lakes (with hardness above 2000 mg/L) and ponds of Kancheepuram district, Tamilnadu were inoculated with a mixture of micro algae, *Chroococcus turgidus*, *Cylindrospermum majus*, *Nostoc muscorum*, *Chlamydomonas elegans*, *Scenedemus bijugatus*, and *Tetraedron caudatum*. After 7 days incubation total hardness, calcium and magnesium were analyzed and the results are presented in Tables 8 and 9 and Figs 8 and 9. In all the treatments there was significant reduction in total hardness. The lakes and ponds with higher total hardness exhibited correspondingly higher reduction of hardness. Lakes showed very high total hardness values well above the permissible limits. Algal remediation has brought the values down to permissible

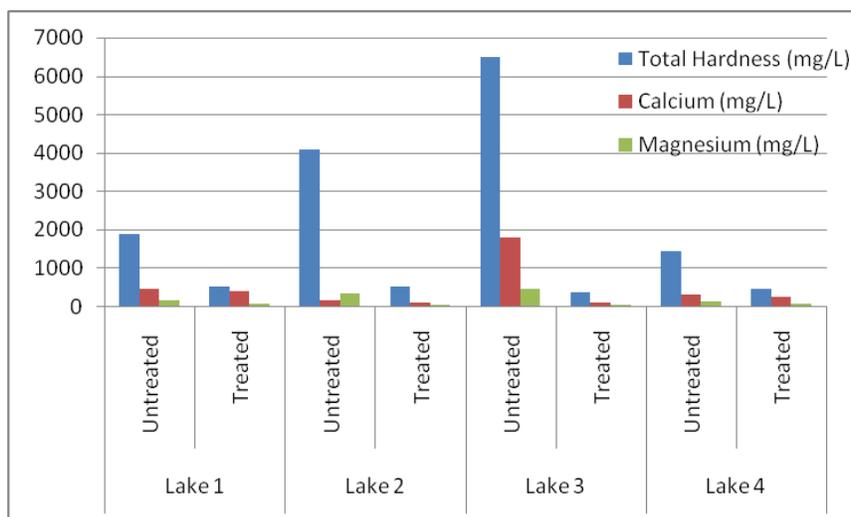
levels (<600). There was a significant reduction in Mg<sup>2+</sup> values when treated with algae (37 to 90% in lake water samples). Although the pond water samples did not exhibit higher total hardness values algal treatment has reduced the values to 2 digits. This technology will yield much better results at the large scale treatment systems.

From the results obtained with both natural waters and industrial effluents it is evident that phycoremediation technology can effectively handle hardness and make the water reusable and industrial effluents become more suitable for R/O recycling. Algal technology can be an ecofriendly, cost effective alternative to chemical technology which is too expensive and results in pollution.

**Table 8. Effect on algal treatment on total hardness of waster samples from selected lakes of Kancheepuram District, Tamilnadu – Lab study**

| Parameter (mg/L)      | Lake 1    |             | Lake 2    |             | Lake 3    |             | Lake 4    |             |
|-----------------------|-----------|-------------|-----------|-------------|-----------|-------------|-----------|-------------|
|                       | Untreated | Treated     | Untreated | Treated     | Untreated | Treated     | Untreated | Treated     |
| Total Hardness (mg/L) | 1900      | 540 (71.5%) | 4100      | 540 (86.8%) | 6500      | 400 (93.8%) | 1440      | 479 (66.7%) |
| Calcium (mg/L)        | 472       | 406 (14%)   | 164       | 128 (22%)   | 1820      | 112 (93.8%) | 336       | 266 (21%)   |
| Magnesium (mg/L)      | 173       | 75 (56.6%)  | 346       | 53 (85%)    | 468       | 48 (90%)    | 144       | 91(37%)     |

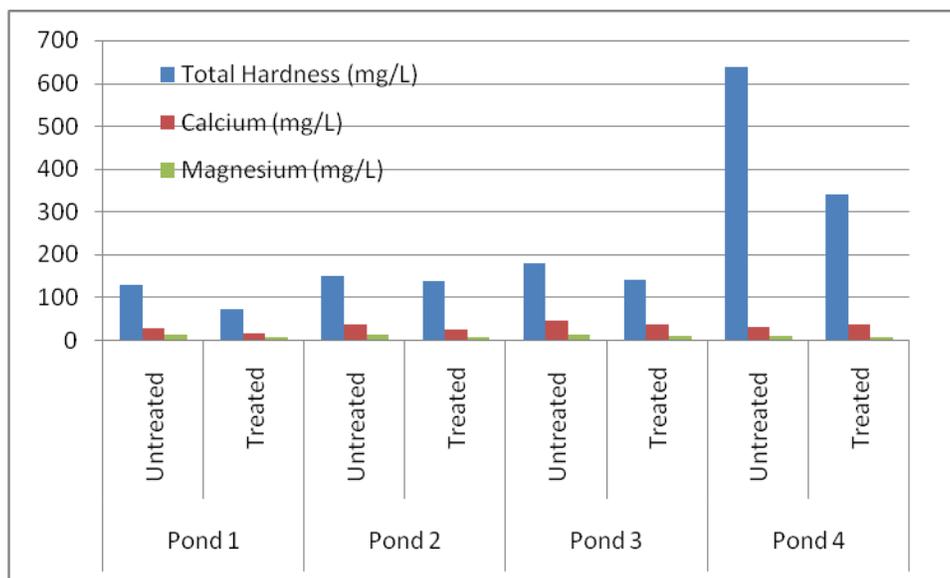
**Fig 8. Effect on algal treatment on total hardness of waster samples from selected lakes of Kancheepuram District, Tamilnadu – Lab study**



**Table 9. Effect on algal treatment on total hardness of water samples from selected ponds of Kancheepuram District, Tamilnadu – Lab study**

| Parameters            | Pond 1    |         | Pond 2    |         | Pond 3    |         | Pond 4    |         |
|-----------------------|-----------|---------|-----------|---------|-----------|---------|-----------|---------|
|                       | Untreated | Treated | Untreated | Treated | Untreated | Treated | Untreated | Treated |
| Total Hardness (mg/L) | 130       | 75      | 152       | 138     | 180       | 142     | 638       | 341     |
| Calcium (mg/L)        | 29        | 19      | 38        | 26      | 48        | 39      | 33        | 38      |
| Magnesium (mg/L)      | 14        | 10      | 14        | 10      | 14        | 12      | 13        | 10      |

Fig.9. Effect on algal treatment on total hardness of waster samples from selected ponds of Kancheepuram District, Tamilnadu – Lab study



## References

Aarathi, N., P.Sumathi, V.Sivasubramanian 2008. Algal treatment (Phycoremediation) to improve water quality. *Indian hydrobiology*, **11**(1):173-184.

APHA, 1985. *Standard Methods for the Examination of Water and Wastewater*. 14<sup>th</sup> Ed American Public Health Association, Washington DC .

Hanumantha Rao, P, R Ranjith Kumar, V V Subramanian and V Sivasubramanian . 2010. Environmental impact assessment of *Chlorella vulgaris* employed in phycoremediation of effluent from a leather-processing chemical industry. *J. Algal Biomass Utiln.* **1** (2): 42 – 50

Hanumantharao, P, R Ranjith Kumar, B Govindaraghavan,

V V Subramanian, V Sivasubramanian 2011. Is phycovolatilization of heavy metals a probable (or possible) physiological phenomenon? - An in situ pilot-scale study at a leather-processing chemical industry. *Water Environment Research*, **83**(4):291-297(7)

Kamaleswari J and V Sivasubramanian. 2011. Role of freshwater algae in remediation of effluents and wastewater. *Indian Hydrobiology*, **13** (2): 94 - 97.

Kamaleswari J, S Murugesan and V Sivasubramanian 2007 Screening of freshwater algae for phycoremediation potentialities of industrial effluents and wastewater. *Eco. Env. & Cons.* **13**(4): 697 – 701

Murali, R, Subramanian, V.V, Sumathi, P. and Sivasubramanian,V. 2009. Studies on kinetics of phosphate uptake by blue-green algae *J. Algal Biomass Utiln.*, **1** (1): 41 – 60.

Ronald L. Droste . 1997. *Theory And Practice Of Water And Waste Water Treatment*, , John Wiley and Son

Sivasubramanian, V. 2006. Phycoremediation – Issues and Challenges. *Indian Hydrobiology* **9** (1): 13 – 22.

Sivasubramanian, V., Sankaran, B., Murali R. and Subramanian, V.V 2011, Micro algal technology to correct pH and reduce sludge in an acidic effluent from a detergent industry. *J. Algal Biomass Utiln.*, **2** (1): 95 – 102.

Sivasubramanian, V, V.V. Subramanian, B.G. Raghavan and R. Ranjithkumar 2009 Large scale phycoremediation of acidic effluent from an alginate industry. *ScienceAsia* **35**: 220-226

Sivasubramanian, V, V V Subramanian and M Muthukumaran. 2010. Bioremediation of *chrome-sludge*

from an electroplating industry using the micro alga *Desmococcus olivaceus* – A pilot study. *J. Algal Biomass Utiln.* **1** (3): 104.128

Sivasubramanian, V, B Sankaran, R. Murali and V V Subramanian. 2011. Micro algal technology to correct pH and reduce sludge in an acidic effluent from a detergent industry. *J. Algal Biomass Utiln.* 2011, **2** (1): 95 – 102.

Venkataraman. L.V. and Becker. E.W. 1985. *In Biotechnology and Utilization of algae – The Indian Experience*. Dept. of Science and Technology, New Delhi, India.