

# A correlation study on reduction of hardness of effluent and phytochemical content of bioremediant

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## ABSTRACT

Leather is one of the major foreign exchange earners in India. Tanning is the process of converting raw hides or skins into leather. Hides and skins have the capability of absorbing tannic acid and other chemical substances that prevent them from decomposing, build resistance to wetting, and keep them flexible and durable. Even though tanneries exist for a long time, the problem of environmental pollution focused seriously only in recent years. The pollutants of tanneries in the country produce significant damage in drinking water supply and irrigation. In this study, leather effluent was treated with various marine algal extracts to reduce the hardness.

In this study, seaweeds such as *Centeroceras clavulatum*, *Enteromorpha flexuosa*, *Grateloupia lithophila*, *Enteromorpha intestinalis*, *Chaetomorpha antennina* and *Ulva lactuca.*, were collected from Covelong, Chennai. *Sargassum sp.*, *Amphiroa sp.*, *Ulva sp.*, and *Hypnea sp.* were collected from Kanyakumari and *Chaetomorpha antennina* was collected from Puducherry. These seaweeds were underwent extraction with various solvents such as methanol, ethanol, water, chloroform and benzene. The extracts were then used to treat effluent. After treatment, the reduction in hardness was estimated. Results revealed that the maximum hardness reduction was obtained by ethanolic extract of *Hypnea sp* collected from Kanyakumari (83%) and the lowest was found in methanolic extract of *Grateloupia lithophila* collected from Covelong (27%). Then these reduction results were correlated with phytochemical constituents of algal extracts.

**Keywords:** Seaweed, leather, effluent, solvent extract, hardness, reduction.

## 1. INTRODUCTION

Water becomes hard by being in contact with soluble, divalent and metallic cations. The two main cations which cause water hardness are calcium and magnesium. Calcium is dissolved in water when it passes over and through limestone deposits. Magnesium is dissolved as water passes over and through dolomite and other magnesium bearing formations. Since groundwater is in contact with these geologic formations for a longer time than surface water, it is usually harder than surface water. Hardness was actually defined as the capacity of water to precipitate soap. Calcium and magnesium precipitate soap, forming a curd which causes bathtub ring and yellowing, loss of brightness, graying, reduced life of washable fabrics and feels unlikable on the skin.

Organic pollutants and heavy metals are found to be a serious environmental problem for human health (Filip et al., 1979). The contamination of soils and aquatic life systems by toxic metals and organic pollutants has increased day to day due to anthropogenic activity.

Removal of hardness by chemical method involves chemical water softeners. There are two types of water softening; those which lead to precipitation; and those that do not precipitate. The use of magnetic treatment was reported in the United States since 1975 (Grutsch & McClintock, 1984) and in other parts of the world for many years (Kobe et al., 2001). Magnetic water treatment (MWT) plays an important role among chemical water softening methods regarding scale control and separations of dispersed solid particles (Lipus et al., 2001). A laboratory based study tested the effect of treating solutions and particulates of CaCO<sub>3</sub> with magnetic effect on precipitation (Kney and Parsons, 2006). But there is relatively little scientific literature on magnetic water treatment and also it is not clear how this method works (Coe and Cass, 2000).

Phytoremediation is an emerging technology which uses plants for removal of environmental pollutants or detoxification to make them harmless (Nakajima et al., 1981). Many living organisms can build up certain toxicants to body concentrations much higher than present in their environments (Ting et al., 1989). Hence the use of plants for decontaminating heavy metals has attracted the attention because of several problems associated with pollutant removal using conventional methods. Bioremediation strategies have been proposed as an alternative due to their lower cost and higher efficiency (Hassett et al., 1981).

Algae based remediation technology can provide solution for pollution problems. Application of algal technology was used to reduce total hardness in waste waters and industrial effluents. In this study algal extracts were used to treat leather effluent.

## 2. MATERIALS AND METHODS

**Collection works:** Marine algal sample used in this study were collected from coastal regions of Tamil Nadu and Puducherry. Marine algal species such as *Centeroceras clavulatum*, *Enteromorpha flexuosa*, *Grateloupia lithophila*, *Enteromorpha intestinalis*, *Ulva lactuca.*, and *Chaetomorpha antennina* were collected from Covelong, Chennai. *Sargassum sp.*, *Amphiroa sp.*, *Ulva sp.*, and *Hypnea sp.* were collected from Kanyakumari and *Chaetomorpha antennina* from Puducherry. They were identified by Dr.M.Baluswamy, Professor and Head, Department of Plant

biology and Plant Biotechnology, Madras Christian College, Chennai. Then the seaweeds were completely washed with water to and were dried under sun light. Then the dried algae were powdered well using a mixer and stored. Leather industries effluent was collected from Nagalkeni village, Pallavaram, Chennai, Tamil Nadu where most of the leather industries are located. Then it was preserved in a refrigerator to avoid further contamination.

**Preparatory work:** Powdered seaweed were soaked in solvents in the ratio of 1:10 and left for 2 days for non-polar solvents (benzene and chloroform) and one day for polar solvents (methanol, ethanol and water). Table.1 shows the various extracts of seaweed and their abbreviations used in this study for convenience.

**Table.1. Seaweed extracts using in this study**

Name of Seaweed	Collection Place	Chloroform	Water	Benzene	Methanol	Ethanol
<i>Enteromorpha intestinalis</i>	Covelong	EICC	EIWC	EIBC	EIMC	EIEC
<i>Ulva sp.</i>	Kanyakumari	UCK	UWK	UBK	UMK	UEK
<i>Hypnea sp.</i>	Kanyakumari	HCK	HWK	HBK	HMK	HEK
<i>Grateloupia lithophila</i>	Covelong	GLCC	GLWC	GLBC	GLMC	GLEC
<i>Sargassum sp.</i>	Kanyakumari	SCK	SWK	SBK	SMK	SEK
<i>Chaetomorpha antennina</i>	Puduchery	CACP	CAWP	CABP	CAMP	CAEP
<i>Centerocerus clavulatum</i>	Covelong	CCCC	CCWC	CCBC	CCMC	CCEC
<i>Ulva lactuca</i>	Covelong	ULCC	ULWC	ULBC	ULMC	ULEC
<i>Enteromorpha flexuosa</i>	Covelong	EFCC	EFWC	EFBC	EFMC	EFEC
<i>Chaetomorpha attenina</i>	Covelong	CACC	CAWC	CABC	CAMC	CAEC
<i>Amphiroa sp.</i>	Kanyakumari	ACK	AWK	ABK	AMK	AEK

**Qualitative analysis of phytochemical constituents:** Phytochemical constituents of algal extracts such as Terpenoids and Triterpenoids (Salkowski and Ernst Leopold, 1904), Phenol (Mace, 1963), Flavonoids (Sofowora, 1993), Tannins (Segelman, 1969), Aminoacid (Yasuma and Ichikawa, 1953), Carboxylic acid (Harborne, 1998), Glycoside (Ramakrishnan, 1994), Cardiac glycoside (Harborne, 1998; Kokate, 2001), Anthraquinone (Trease and Evans, 1997), Carbonyl group (Venkatesan, 2009), Saponin (Kokate, 1999), Coumarin (Kiran Kumari, 2012), Phlobatanin (Pravin, 2012) were analyzed.

**Treatment of Effluent and Analysis of hardness:** Algal extract and effluent were mixed in the ratio of 1:10 and treated for 5 days. After five days, hardness of water was analyzed (Kotaih and Swamy, 1994).

### 3. RESULTS AND DISCUSSION

In this study, the total hardness of untreated effluent was found to be 3000 mg/l which was very much higher than the permissible limit of EPA (Table.2).

**Phytochemical analysis of algal extracts:** Phytochemical analysis showed that the terpenoids were absent only in EIEC, UEK, SEK, GLEC, CCCC and CCWC. Aqueous extracts showed absence of carboxylic acid except in *E.intestinalis* collected from Covelong and in case of chloroform extracts it was found only in ULCC and CACP. Seven extracts of ethanol showed presence of carboxylic acid except EFEC, CCEC and AEK. Phytochemical report showed that most of the extracts contained carbonyl compounds except in UEK, CAEP. HEK, AEK, CAEC, HMK, CAMP, CCMC, GLMC, UMK, CACP, CCCC, CACC, ACK, HWK, GLWC, EIWC. All the methanolic extracts showed presence of carbonyl compounds. Phenol was found to be absent in the aqueous extracts such as CAWC, ULWC, AWK, UWK, CCWC, HWK, GLWC, SWK and also in methanolic extracts of *Chaetomorpha sp.*, from Covelong and *Amphiroa sp.*, from Kanyakumari. Since solubility of phenol is very less at room temperature. All the aqueous extracts showed presence of aminoacids and it was found to be absent in all benzene extracts except in EFBC and also absent in chloroform extract except in EFCC. Because of high solubility of amino acids in water and its solubility decreases towards non polarity (Thomas, 1970). Other extracts showed presence of amino acid except in ULEC, CACP, AEK, CAEC, HMK, SMK, CAMP, ULMC, EIMC, GLMC, and UMK. (Data not shown).

**Hardness reduction and its correlation with phytochemicals:** After treatment, the reduction efficiency was categorized as A, B and C (Table.3). The treated effluent showed maximum reduction in hardness by the algal extracts. There were thirteen algal extracts which showed good reduction (Fig.1) and were listed under Category A.

Hardness was reduced in tannery effluent by the extracts of *Prosopis juliflora* (Sharmila, 2013a) which was almost closer to this study result.

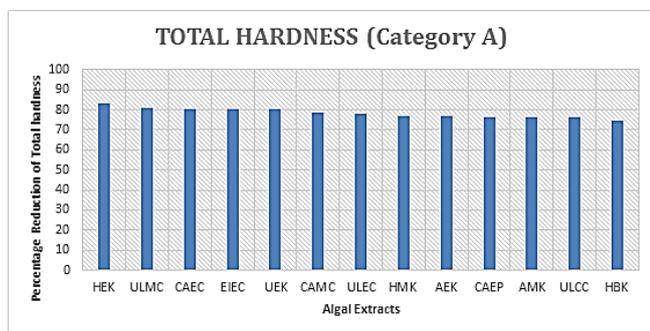
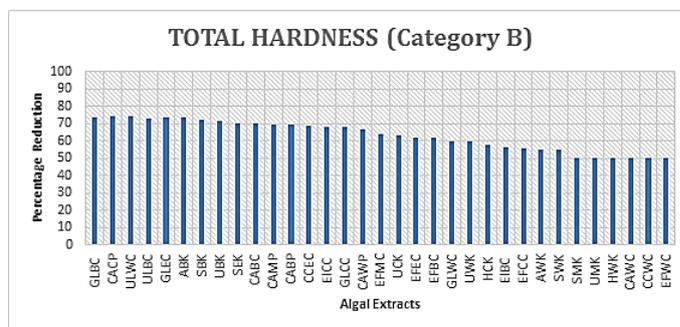
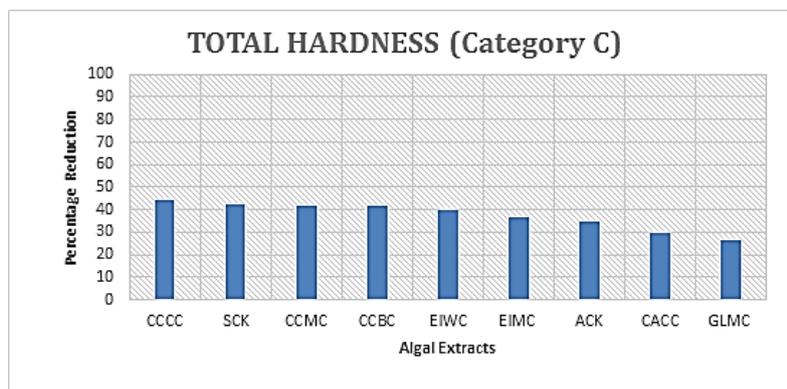
**Table.2.EPA Classification of water hardness**

Hardness	mg/l as CaCO <sub>3</sub>
Soft	0 to 50
Moderately hard	50 to 150
Hard	150 to 300
Very Hard	Above 300

More extracts fallen under Category B type reduction (Fig.2) while few extracts showed poor reduction (Fig.3). Methanolic extract of *Annona squamosa* considerably reduced hardness of paint industry effluent (Sharmila et al., 2013b). Cecilia Rolence (2014) stated that the hardness removal efficiency of coconut shell activated carbon was 60 % which was comparatively lower than this study.

**Table.3.Categories of Reduction**

Category	Percentage Reduction	Remark
Category A	75 % - 100 %	Good
Category B	50 % - 75 %	Medium
Category C	Below 50 %	Poor

**Fig.1.Percentage Reduction in Total Hardness (Category A)****Fig.2.Percentage Reduction in Total Hardness (Category B)****Fig.3.Percentage Reduction in Total Hardness (Category C)**

Micro algal cultures of *Chlorococcum humicola* were inoculated into the effluent samples and the results showed 87 % reduction of total hardness. From the results obtained with both natural water and industrial effluents it is clear that phycoremediation technology can effectively handle hardness and make the water reusable and industrial effluents become more suitable for recycling (Sivasubramaniam et al., 2012). While using *Synechocystis salina* almost 78 % of total hardness reduction was achieved in 15 days of treatment (Anteneh and Omprakash Sahoo, 2014) which was equivalent to this research but reduction could be attained more effectively within five days of treatment.

This study has shown that the presence of carboxylic acid might have been the reason for the reduction of hardness. Carboxylic acids react with metal carbonate such as calcium or magnesium carbonate and produce salt, water and carbon dioxide (WWW, 8). This salt solubilizes in water. However there are no reports to justify the statement, it might be the reason for the reduction of hardness. It also reduces the fluoride level in water and also act as antifoaming agent. It has been shown that the ethanol was the good solvent system in the reduction of hardness in

which carboxylic acid and carbonyl compounds were present except for *Amphiroa sp.* Among all the sample *Ulva lactuca* and *Enteromorpha flexuosa* collected from Covelong was found to be the best since all the extracts came under Category A type reduction and *Centeroceras clavulatum* extracts reduced less hardness since carboxylic acids were absent in CCCC, CCBC and CCMC

#### 4. CONCLUSION

Using of algal technology for treating effluent is an upcoming technology to reduce harmful contents present in the effluent. Furthermore studied has to be carried out in future to bring it to highly economical one.

#### ACKNOWLEDGEMENT

Authors are thankful to Bharath University for carrying out this research work and also thankful to Dr. M. Baluswamy, Professor and Head, Department of Plant biology and Plant Biotechnology, Madras Christian College, Chennai for identifying all the seaweed sample of this research project.

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