Comparative Study of Phytoremediation and Microalgae Technology for Treatment of Emulsified Organic Effluent

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Abstract - The main focus of the project was on designing an effective secondary biological treatment using bioremediation techniques. A suitable primary treatment was also carried out on the effluent. The raw effluent used for the study was taken from an organic chemicals industry that specializes in producing surfactants. The basis of the project was wastewater treatment with an objective of overcoming the shortcomings of the current effluent treatment plant at the industry. The key features of the treatment undertaken were: (i) Breaking of emulsion, neutralization, flocculation and filtration as part of the primary treatment. (ii) A multi-dimensional secondary treatment which encompassed a detailed characterisation before and after the treatment; a comparative analysis of phytoremediation and microalgae technologies. (iii) Making it as cost-effective as possible.

Keywords – Chemical effluent, Bioremediation, Wastewater treatment, Phytoremediation, Water hyacinth, Microalgae technology, *Chlorella.*

Introduction: Industrial wastewater is the aqueous discard that results from the use of water in an industrial manufacturing process or the cleaning activities that take place along with that process. [1]

The strength of waste water is normally measured using accurate analytical techniques. The more common analyses used to characterise wastewater entering and leaving a plant are:

- BOD_5
- COD
- TSS
- pH
- Total phosphorus
- Total nitrogen [2]

Wastewater treatment can involve physical, chemical or biological processes or combinations of these processes depending on the required outflow standards.

The first stage of wastewater treatment takes place in the preliminary treatment plant where material such as oils, fats, grease, grit, rags and large solids are removed. 'Chemical treatment' is used to improve the settling abilities of suspended solids prior to a solids removal stage or to adjust the properties or components of wastewater prior to biological treatment. 'Biological treatment' of waste waters takes place in fixed media or suspended growth reactors using activated sludge, biofiltration, rotating biological contactors, constructed wetlands or variants of these processes. 'Tertiary treatment' refers to processes which are used to further reduce parameter values below the standards set out in national regulations. The term is often used in reference to nutrient removal. [2]

This paper focuses on primary and secondary treatment of effluent from organic chemicals industry.

The company is engaged in manufacturing the surfactants, which are mainly used as Emulsifiers, for the various applications. These surfactants are Non-Ionic Surfactants, Cationic Surfactants, Anionic Surfactants and Amphoteric Surfactants.

Research Approach: The objectives of the project were to carry out a complete characterization of the effluent at every step of the treatment to understand its complete composition and to make the selected treatment as efficient as possible in terms of cost, time and quality.

Since, the effluent obtained was a high molecular weight emulsion, the following approach was used for treating the effluent:

Breaking Emulsions: Chemical demulsification is very complex. Demulsifiers displace the natural stabilizers present in the interfacial film around the water droplets. This displacement is brought about by the adsorption of the demulsifier at the interface and influences the coalescence of water droplets through enhanced film drainage.

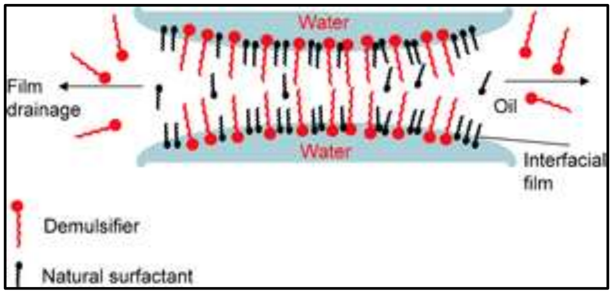

Fig. 1: Film drainage in the presence of a demulsifier. The demulsifier displaces the indigenous surfactants in the interfacial film. [3]

Chemical Demulsifiers like Salt, vinegar, glycerine, alcohol, hexane can be used to break emulsions [4] [5] [6] because they break the interfacial film formed between the oil and water by replacing themselves in place of the surfactants. [7] [8] [9] Out of the above mentioned chemicals, salt works out to be the best demulsifier. Temperature is extremely important. 90 ^{0}C (195 ^{0}F) is the ideal temp for washing any oil/water batch. It greatly reduces the chances of making an emulsion.

Working of salt:

Salt is insoluble in oil but highly soluble in water. Salt actually has an extreme affinity to water and no affinity for oil. Also, salt is very cheap.

There are a lot of things that affect emulsions; here are a few of the basics :

(i) Difference in Densities- The greater the difference between the two densities, the easier two fluids will separate into two distinct layers.

(ii) Viscosity- As oil is heated, they become less dense. However, it also decreases the oil's viscosity.

(iii) Salt (NaCl) increases the ionic strength of the aqueous layer. [5]

(iv) Oil-wet solids stabilize water-in-oil emulsions. Water-wet solids can also be made oil-wet with a coating of heavy polar materials and can participate effectively in the stabilization of water-in-oil emulsions. [10][11] High pH, therefore, helps in destabilizing water-in-oil emulsions. It has also been reported that basic pH reduces demulsifier dosage requirements. [12]

Residence time: Typically it is between 10 to 30 minutes for normal crude oil production; however, it may need to be much longer to treat tight emulsions effectively.

Now, the conventional primary treatment can be carried out, which would include liquid- liquid separation[13], sedimentation[14] [15], neutralization[16], flocculation[17] [18] [19] and filtration.[20]

This primary treatment was then followed by a secondary treatment. In the biological treatment of wastewater, a mixed population of microorganisms utilizes the colloidal and dissolved organics found in the effluent from the primary treatment as their main food supply.

This project was based on the following 2 biological treatment methods:

Phytoremediation is the use of vegetation for in situ treatment of contaminated soils, sediments, and water.

Plants have shown the capacity to withstand relatively high concentrations of organic chemicals without toxic effects, and they can uptake and convert chemicals quickly to less toxic metabolites in some cases. [21]

The plant used for phytoremediation in the project was the Water Hyacinth (*Eichhornia crassipes*). Water hyacinth is a free-floating perennial plant that can grow to a height of 3 feet. Water hyacinth was found to effectively reduce the levels of suspended particles, dissolved impurities, other pollutants, BOD, COD, turbidity etc. According to Wilson et al. (2001) there are five main factors limiting the growth rate and carrying capacity of water hyacinth: salinity, temperature, nutrients, disturbance and natural enemies. [22]

Microalgae play a vital role in the assimilation of pollutants in natural water systems. The mass culture of microalgae in wastewater can significantly contribute to the management of water ecosystems by providing an inexpensive, environmentally sound addition (in cases of relatively heavy pollutant loading situations) or alternative (in cases of relatively light pollutant loading situations) to conventional energy intensive wastewater treatment systems. The major advantage mass cultured microalgae has over conventional aerobic wastewater treatment systems is reduced cost due to the decrease in energy input. [23]

Materials and Methods: The effluent was first characterized for the basic parameters: pH, Conductivity, Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Oil & Grease (O&G), Chemical Oxygen Demand (COD) & Biochemical Oxygen Demand (BOD) using APHA methods.

A stage wise treatment was undertaken to assess the treatability of the effluent.

The steps involved in this procedure are as follows:

1. First, a sedimentation tank was designed for proper settling and separation.
2. After considering the salinity limits for the species that would be used for secondary treatment, the concentration of salt to be used for demulsification was calculated. Salinity limit for microalgae *Chlorella* species is 30 g/l. Thus, 30 grams of salt in solution with tap water was used for breaking the emulsion in 1 litre of wastewater.
3. The salt solution was added intermittently in small amounts and vigorous stirring and shaking was done after each addition.
4. This set up was allowed to stand for 24-48 hours depending on the quantity of water for proper phase separation. Better separation was observed for longer standing time.
5. The sludge thus formed was removed using a muslin cloth via double filtration.
6. Now, neutralization of the effluent was done using concentrated sulphuric acid (98%) since the original pH of the effluent was 11.23.
7. 5-7 drops of 0.1% polyelectrolyte solution per litre of wastewater was added drop wise, with intermittent mixing for proper coagulation to increase ease of separation.
8. After settling, filtration was carried out again using muslin cloth and the effluent was stored at 4^0 C until further use.
9. This process was tested for 50, 100, 200, 500, 1000, 2000, 3000 ml of wastewater. Characterization was done at every step of scale-up to ensure effectiveness of the method.

Fig. 2: Formation of Sludge post 24- 48 hrs standing time

<u>Secondary Treatment:</u>

The primary treated water obtained was further treated using two different secondary biological treatment methods viz. Phytoremediation and Microalgae technology.

Phytoremediation:

A. General procedure for phytoremediation:

1. Water hyacinth plant was procured from already growing source and grown in fresh water for some time.
2. The assembly for the treatment was constructed using a shallow tray about 15-20 cm deep. A layer of sand and gravel was laid at the bottom of the tray for trapping the suspended solids and obtaining better clearance.

3. Initial readings of the primary water for BOD, COD, pH, conductivity, oil & grease, TDS, TSS were measured.
4. To check the concentration at which hyacinth works the best, dilutions of 250 ml, 500 ml, 750 ml and 1000 ml of waste water were kept. (This was done to check if it was the concentration of primary water or the toxicity of contaminant absorbed by the hyacinth which affected its growth.)
   (It was observed that the texture of the leaves changed from turgid to flaccid and colour turned lighter post 5 days. Also, a reduction was observed in parametric values.)
5. Accordingly, primary water was diluted to 50% with tap water. About 6 litres of this was added to the assembly. A small amount of fertilizers (NPK and urea) were added to the water initially to aid the growth of the plant.

Fig. 3: Phytoremediation using Water hyacinth

6. After every 5 days, the above mentioned tests were carried out again till 15 days.
7. Fresh plant were introduced to enhance activity and kept in same conditions as before whenever required.
8. The plant was separated from the water and disposed.

Microalgae Technology:
Procedure:

1. Pure culture of *Chlorella pyrenoidosa* was obtained from NCIM.
2. A part of the master culture was first used to make saline suspension and used to inoculate flasks containing Fog's media (without agar). This was allowed to grow for 15 days.
3. Next, to acclimatize the algae to the wastewater, the wastewater was cumulatively added in increasing concentrations (starting with 10% wastewater) along with the fog's media (without agar) after every 3-5 days to the microalgae. This was done upto 50% dilution.
4. The algae were separated from the media flasks by filtration with Whatmann filter paper. 2 ml of uniform suspension of *C. pyrenoidosa* was taken as initial inoculums and a measured amount (obtained by filtering the mass from 2-3 flasks) was inoculated in the flasks in increasing concentrations for a month.
5. Finally, the sample was transferred to a bigger assembly having a 50:50 ratio of Fog's media to wastewater. This was considered to be the 0th day for the treatment period of 15 days. The concentration was kept fixed and the action of microalgae on the wastewater was observed for the next 15 days by carrying out a detailed characterisation of the wastewater parameters after every 5 days.
6. The experiment was conducted under controlled conditions (temperature 27 ± 2 ^{0}C) at 100-300 lux intensity for a total duration of 15 days. A regular observation of the culture viability was carried out by viewing the microalgae under the microscope.
7. An aliquot of sample was drawn from the assembly and periodically (every 5th day) analysed for physico-chemical parameters such as pH, conductivity, Oil and Grease, TDS, BOD and COD using standard methods (APHA).
8. At the end of 15 days, the microalgae were separated from water by filtration and oven dried to powder form and discarded. The water was sent for tertiary treatment. (or algal biodiesel in future prospects)

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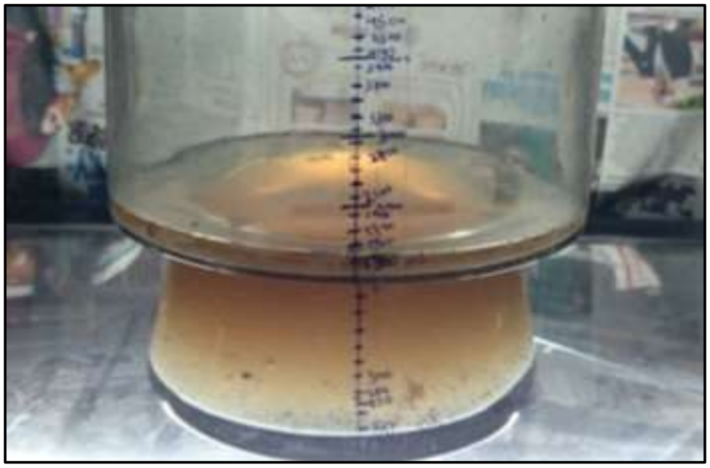

Fig. 4: Treatment using microalgae technology

Results: Following results were obtained during the course of treatment:

Table 5.1 Detailed stepwise reduction obtained in each parameter by both technologies

PARAMETERS		pH	Conductivity (mS/cm)	Oil & Grease (mg/L)	TDS (mg/L)	TSS (mg/L)	COD	BOD
RAW EFFLUENT		**11.23**	**14.7**	**90,030**	**8060**	**7684**	**2,01,060**	**64,800**
PRIMARY TREATED		**7.27**	**33**	**482**	**19,800**	**636**	**30,400**	**6450**
POST SECONDARY TREATMENT								
With Hyacinth	**DAY 0**	**7.27**	**20.2**	**240**	**12,329**	**712**	**29,600**	**6200**
	DAY 5	**7.29**	**19.7**	**120**	**11,840**	**700**	**13,600**	**3300**
	DAY 10	**7.86**	**19**	**87**	**11,400**	**333**	**10,217**	**2870**
	DAY 15	**7.66**	**18.2**	**60**	**10,920**	**246**	**7920**	**1050**
With Micro Algae	**DAY 0**	**7.49**	**22.3**	**63**	**13,380**	**NA**	**24,400**	**4950**
	DAY 5	**7.56**	**23.1**	**35**	**13,860**	**NA**	**24,000**	**3450**
	DAY 10	**7.58**	**18.7**	**10**	**11,220**	**NA**	**13,200**	**2400**
	DAY 15	**7.23**	**14.3**	**3**	**8,580**	**NA**	**7200**	**1350**
CPCB LIMITS REQUIRED POST TERTIARY TREATMENT								
CPCB LIMITS (All maximum)		**6.5-8.5**	**-**	**10**	**100**	**100**	**250**	**100**

Comparative study of Phytoremediation and Microalgae technology through 15 days of treatment:

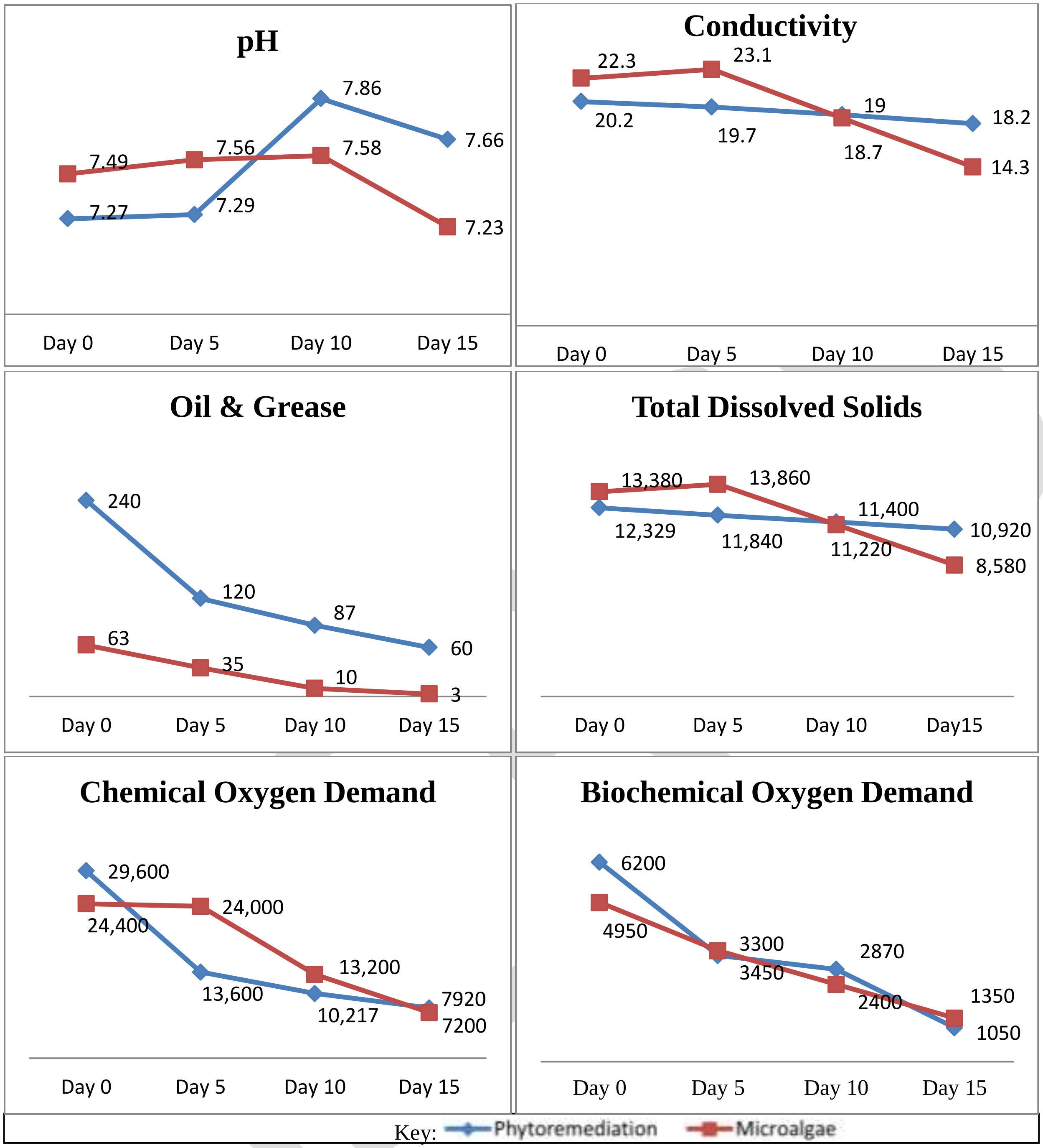

Fig. 5.7: Graph showing variation in various parameters

Discussion: The basis of the project was wastewater treatment with an objective of overcoming the shortcomings of the current effluent treatment plant of the organic chemical factory from where the effluent was taken. Though the main focus of the project was on designing an effective secondary biological treatment, a suitable primary treatment was also carried out on the effluent. The key features of the treatment undertaken were: (i) Breaking of emulsion, neutralization, flocculation and filtration as part of the primary treatment. (ii) A multi-dimensional secondary treatment which encompassed a detailed characterisation before and after the treatment; a comparative analysis of phytoremediation and microalgae technologies and making it as cost-effective as possible.

An overview of the reduction in the parametric values over the entire duration of the treatment is indicative of the accomplishments of the project. The parameters considered were pH, conductivity, oil and grease, TDS, TSS, COD and BOD. pH was maintained around 7-8 during the course of the treatment. The increase in the conductivity and TDS post the primary treatment due to addition of salt was also tried to be kept under check. There was a drastic decline of 99% in the amount of oil and grease by both the technologies. Phytoremediation led to a decrease of 96.79% in the TSS value of the effluent, while the TSS value wasn't taken under consideration because of the interference by microalgae. Finally, the highlight of the treatment was the remarkable reduction observed in the COD and BOD by both the technologies viz.; 96.03% and 98.37% reduction in the COD and BOD values, respectively by Phytoremediation, 96.4% and 97.91% reduction in the COD and BOD values, respectively by Microalgae technology. Further, an appropriate tertiary treatment is to be performed to meet the acceptable values by CPCB for disposal. Possible suggestions are passing the treated effluent through pressure sand filter and activated carbon filter to eliminate odour and colour. Also, performing an electrodialysis or reverse osmosis for de-salting which will effectively reduce the conductivity and TDS.

Cost Analysis: The objective of the installation and operation of wastewater treatment systems is to assure an environmentally friendly effluent quality meeting the determined border values in a creative, cost-effective and environmentally sound way. The costs involved in constructing and operating a wastewater treatment plant can be broadly divided into two categories: (1) investment costs and (2) operating expenses. [24]

After consulting the company, it was noted that the costs incurred by the company are Rs. 1-2 for primary and secondary treatment; and Rs. 2-3 for tertiary treatment per litre of water. The expenses for our suggested treatment will primarily include the cost of the raw materials and operational charges. The raw materials required in the primary treatment were salt (Rs.10/kg), conc. sulphuric acid (Rs.500/litre), and polyelectrolyte (Rs.280/kg). The secondary treatment includes the raw materials water hyacinth (Rs.2/per plant) and microalgae (starter culture obtained from NCIM and then sub cultured). Thus, the cost per litre won't exceed Rs.2-2.5 for the primary and secondary treatment which is within the budget of the company.

Future Prospects: The main future application of the project is the scale-up of the treatment at the industrial level. The company under our consideration requires nearly a 100 fold scale-up. The main factors to be considered during the scale-up of the treatment involve: (1) Area required for set-up (2) A sedimentation tank (3) Maintaining appropriate conditions for biological treatment on a large scale and (4) Disposal of sludge and biological waste.

The primary treated water at high concentrations can prove detrimental to the growth of the organisms in the secondary treatment. Hence, dilution is required. Initially, water can be added to the treatment plant. Then, this batch of effluent after treatment post 15 days can be recycled to dilute the next batch of effluent to be treated. In this way, the wastewater can be effectively utilized without any wastage or need of more water for dilution.

Since, both the technologies have their limitations in terms of space required and maintenance; a combination of these technologies might help to mask the shortcomings and may give better results. Either phytoremediation can be followed by microalgae treatment or both of them can be used simultaneously to give enhanced and quicker results.

One of the most significant aspects to be considered at a large scale is disposal of sludge generated, water hyacinth and microalgae post treatment which can be used in compost, landfills or to make biodiesel.

Conclusion: At the end of this endeavour, we have successfully devised two treatment options. Post implementation necessary troubleshooting can be done. Further research on this subject matter is imperative since such 'green' technologies are the need of the hour and the Governments especially in developing countries like India are willing to invest in innovative substitutes. Though these technologies require a lot of investment in terms of extensive research and development, time and capital; but upon culmination it will be rewarding.

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