Macro algae based adsorption for treatment of cotton processing wastewater

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Abstract: In the recent advances in treatment of different industrial wastewater, an attempt is made to treat the wastewater produced in demand of dyes and is used to make bandages and surgical cotton using freshwater macro algae. In the treatment method adopted here is focused on reducing the organic and inorganic pollutants present in the wastewater in the form of COD, BOD, Nitrate, Ammonia, Phosphate and Sulphate. Cotton processing wastewater contains high level of tCOD and sCOD in the order of 15000. Initially, Fresh water Green Macro algae is grown in freshwater Bold's Basal Medium (BBM). Tests were conducted with different dilution of Medium, Wastewater and Macro algae. The concentration of COD, NO₃, NH₄, PO₄, and SO₄ in the real wastewater found to be 4800mg/l, 60.236mg/l, 19.132mg/l, and 2.239mg/l respectively. Finally, after 10 days of continuous treatment of cotton wastewater using macro algae was found to be 1600mg/l, 7.30mg/l, 1.970mg/l, 4.800mg/l, and 1.009mg/l respectively. COD concentration of 1600 mg/l was still not a safe value to be finalized for a safe disposal, it has been observed that due to the high toxicity of the wastewater, macro algae are unable to treat the wastewater further. Solids like Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Fixed Solids (FS) and Total solids (TS) are also noted and studied during the treatment.

1. INTRODUCTION

Water culture in engineering aspects of wastewater treatment, recycling and reusing has received increased interest nowadays. The water treatments facilities are designed to achieve specific and particular wastewater treatment and wastewater objectives and can also solve the environmental and sanitary problems and may also be economically efficient (Humenik & Hanna, 1971)[5]. Due to the day today life of human being in contribution to rising domestic eutrophication in water forming diseases. Due to the production of more quantity of real untreated domestic wastewater in urban and semi-urban areas, using this waste water as a food source present in the form of nutrients for algae feedstock production is an attractive and advanced option to reduce the biodiesel production costs (Chen, et al., 2012)[10]. In India nearly 75% of domestic wastewater released is not treated due to improper connection to treatment plant facilities and lack of adequate facilities for decentralized wastewater treatment systems leading to bad odour. Biofuels produced from the cultivation of algae have therefore been introduced as an additional approach that does not have any bad effect on
agriculture (Craggs, Davies-Colley, Tanner, & Sukias, 2003) [4]. Some of the methods under the thermochemical conversion processes are as hydrogenation, liquefaction, and gasification etc. of algal biomass to get gas- or oil-based biofuels. Biological with chemical called biochemical conversion processes include fermentation and anaerobic digestion of biomass to produce bioethanol or methane. Many species of macro algae are able to successfully grow in wastewater conditions through their ability and adaptation to utilize organic carbon and inorganic N and P in the wastewater (Aslan & Kapdan, 2006) [6]. The use of algae in wastewater treatment has been long promoted (Borowitzka, 1991) [2]. However, chemical processing of waste water or the generation of activated sludge is the conventional and advanced treatment method (Colak & Kaya, 1988) [9]. Although the application of algae in the wastewater industry is still fairly limited due to the conditional growth, algae are used throughout the world for wastewater treatment only at minor scale (Oswald & Golueke, 1968) [1]. That is either through the use of natural oxidation (stabilization) ponds or the more developed suspended algal ponds such as high-rate algal ponds (HRAP) which are shallow raceway-type oxidation ponds with mechanical motor mixing, and have been shown to be highly effective and economic for wastewater treatment (Craggs, Davies-Colley, Tanner, & Sukias, 2003) [4]. Algae and bacteria have a mutually beneficial relationship due to the limited CO2 and O2 needed for respiration of algae and bacteria. CO2 from bacteria is useful for the growth of algae and O2 from algae activity is useful for bacterial growth (Humenik & Hanna, 1971) [5]. Most of the works and studies have been done previously are with various industrial wastewater and domestic wastewater treated with microalgae (Clarens, Resurreccion, White, & Colosi, 2010) [8]. In this research the main focus is on reducing the concentration of Chemical Oxygen Demand (COD) of cotton processing wastewater with Macro algae (Petrie, Barden, & Kasprzyk-Hordern, 2015) [3].

2. MATERIALS AND METHODS

2.1. Cotton processing wastewater collection and characteristics
It was collected from an industry located at chattedrapatty village in viruthunagar district, Tamilnadu, India. And knowing the list of chemicals being added in the process system in making of cotton. To know the level of toxicity and the concentration of various chemicals and nutrients present, the crepe cotton wastewater has to be characterized well before proceeding to treatment. The physical and chemical characteristics of the wastewater (pH, COD, BOD, TSS, TDS, TS, FS, Sulphate, Nitrate, Phosphate, Ammonia, Alkalinity and Hardness) was analyzed by the methods suggested in APHA 2008.

2.2. Collection of freshwater Macro algae
Getting freshwater macro algae from a pond or lake, making sure about the separation and removal of impurities present with the macro algae and collecting only the greenish fine structured long fresh algae for better results. Draining the excess water present in the macro algae with the help of a fine net and getting only the dark green algae in use for further usage.

2.3. Growing of Macro Algae
Macro algae collected from the pond were further drained and used it to grow in lab scale for at least 7 days. Algae in the presence of oxygen supply (aeration) and sun light (fluorescent lamp) were diluted with freshwater and put to grow, the mixture of algae to freshwater were made in the ratio such that the algae starts to grow as soon as possible, throughout the growing stage of algae the pH has to be maintained at 8.0 to 8.5, where the algae are in best situation to grow well and fast.

Finally, after 7 days of stand in process done and then the water drained from the macro algae and weight of algae was measured, found that nearly 20gm of macro algae successfully increased from the initial (2gm) weight of macro algae. There are so many suitable freshwater macro algae mediums available, either readymade or the recipes for the medium to prepare it in lab. The freshwater macro
algae medium chosen in this research is the common and mainly used Bolds Basal Medium, made ready to prepare it in the lab, BBM having stock solutions (table 1) and various trace elements (table 1c) are present, also to be prepared and autoclaved. BBM medium is highly enriched and is used for many of the green algae culture. Combine all trace elements in one standard stock solution. Dissolve each component completely one after the other, autoclaved the whole 1 liter stock. Trace elements solution should not be stored in glass containers, but instead in Teflon or Polycarbonate containers to prevent adsorption of metals to container surface. The preparation is as shown.

| Component                  | Stock Solution (g/l) | Quantity Used (to 1 liter) |
|----------------------------|----------------------|----------------------------|
| NaNO₃                     | 25.00                | 10 ml                      |
| CaCl₂·2H₂O                | 2.50                 | 10 ml                      |
| MgSO₄·7H₂O                | 7.50                 | 10 ml                      |
| K₂HPO₄                    | 7.50                 | 10 ml                      |
| KH₂PO₄                    | 17.50                | 10 ml                      |
| NaCl                      | 2.50                 | 10 ml                      |
| EDTA solution             | See 1(a)             | 1 ml                       |
| Acidified iron solution   | See 1(b)             | 1 ml                       |
| H₃BO₃                     | 11.42 g              | 1 ml                       |
| Trace metals solution     | See 1(c)             | 1 ml                       |

| Component                  | Quantity Used (to 1 liter) |
|----------------------------|-----------------------------|
| EDTA                       | 50.00 g                     |
| KOH                        | 31.00 g                     |

| Component                  | Quantity Used (to 100 ml)  |
|----------------------------|-----------------------------|
| FeSO₄·7H₂O                 | 0.498 g                     |
| H₂SO₄ (96%)                | 0.1 ml                      |

| Component                  | Quantity Used (to 1 liter)  |
|----------------------------|-----------------------------|
| ZnSO₄·7H₂O                 | 8.82 g                      |
| MnCl₂·4H₂O                 | 1.44 g                      |
| MoO₃                      | 0.71 g                      |
| CuSO₄·5H₂O                 | 1.57 g                      |
| Co(NO₃)₂·6H₂O              | 0.49 g                      |

2.4. Treatment Method
The real wastewater is having high level of toxicity and so the treatment of such water is necessary before discharging it anywhere. Knowing that algae are capable of taking any level of toxicity from various industrial wastewater including major nutrients like N and P along with various heavy metals it can consume and convert it into carbohydrates and lipids. Macro algae containing wastewater treatment process requires various factors to be satisfied and for better treatment of reduction in COD.
Medium is the first and important need for algae to survive for long and be active in the process of treating the wastewater. Then, Oxygen supply and the light source (algae naturally works well in sunlight) for oxygen supply we use Aeration system and for light source we have fluorescent light. After preparing the medium, the process system is now ready to treat the wastewater. Putting the wastewater and BBM Medium (medium as prepared in table 1) into the glass aquarium attached with aeration system, making sure that the pH of the medium is 8.0, if not then bring the pH to 8.0 and then add the wastewater into the medium. Medium and wastewater ratio is to be decided in a way that the algae should last longer and must treat the wastewater well, ratio decided here with this wastewater is 1:7, that is, 300ml of wastewater and 2100ml of Medium, after mixing the wastewater and Medium in the ratio provided, the pH of the mixture is in between 9.0 to 9.90, which should be brought to 8.0 before adding the algae into the mixture. Finally to add the Macro algae into the dilution of wastewater and medium.

Florescent lamp on the glass aquarium after closing the lid, Follow the daily routine of controlling the pH at 8.0 and checking the reduction in the values of COD and other major nutrients once in two days (Nitrate, Phosphate, Sulphate, Ammonia) present in the wastewater as the level of treatment test taking place day by day. Note: the pH of the mixture containing wastewater + medium + macro algae to be checked daily and has to be maintained at 8.0 for the algae to grow well.

2.5 Analytical Methods
2.5.1. UV-Spectrophotometer: Liquid samples were analyzed on daily basis using standard methods (APHA, 2005) for Nitrate Sulphate Ammonia and Phosphate at different wavelength for each parameter.

2.5.2 Chemical Oxygen Demand (COD): COD is an important parameter which analyzed to monitor and record the reduction in concentration of the test sample throughout the testing procedure.

2.5.3 Total Organic Carbon (TOC): TOC of the real and filtered wastewater sample was analyzed by a liquid TOC Analyzer (Shimadzu, Japan) as suggested in standard methods (APHA, 2005).

3. RESULTS AND DISCUSSION

As we know about the ability of the algae to give positive result in every industrial wastewater treatment, similarly herein this crepe cotton wastewater treatment also algae (macro algae) have reduced the COD and other nutrients up to a level. As table 2 shows the results of the real wastewater characteristics.

| Table 2. Real Wastewater Characteristics |
|------------------------------------------|
| Parameters                 | Concentration (Mg/l) |                  |
| pH                       | 10.15                |
| COD                      | 4800                 |
| BOD                      | 306.53               |
| Alkalinity                | 3136.5               |
| Hardness                 | 810                  |
| Total solids (TS)        | 12600                |
| Total Dissolved Solids (TDS) | 2480               |
| Total Suspended Solids (TSS) | 58                 |
| Fixed Solids (FS)        | 252                  |
| Nitrate                  | 60.236               |
| Ammonia                  | 4.110                |
| Parameters | Concentration (mg/l) |
|------------|---------------------|
| COD        | 4800                |
| Nitrate    | 60.236              |
| Ammonia    | 4.11                |
| TSS        | 0.040               |
| TDS        | 2050                |
| Phosphate  | 18.257              |
| Sulphate   | 2.239               |

**Table 3. Initial Mixed Wastewater and Algae Characteristics**

| Parameters | Day 1 Conc. | Day 9 Conc. | % Efficiency |
|------------|-------------|-------------|--------------|
| COD        | 4800        | 1600        | 33.33        |
| Nitrate    | 41.41       | 7.3         | 17.63        |
| Ammonia    | 3.47        | 1.97        | 56.77        |
| TSS        | 30          | 47          | NA           |
| TDS        | 1180        | 1420        | NA           |
| Phosphate  | 13.378      | 4.80        | 35.88        |
| Sulphate   | 2.201       | 1.009       | 45.84        |

**Table 4. Wastewater Characteristics during Treatment**

When it comes to any kind of wastewater treatment, COD (Chemical Oxygen Demand) plays an important role in it. COD’s are considered as the most important factor in the treatment of an industrial wastewater, the below figure 1 shows the reduction in COD concentration as the process works day by day. Here, in this project the focus mainly in the reduction of COD of the crepe cotton wastewater which is high when compared to municipal and domestic wastewater, so with the discussion on the result of the treatment system as tabled above. The value of real crepe cotton wastewater COD is 4800mg/l as characterized above (Table 3) and the same COD value after the treatment test, has started to reduce day by day, it is 4800mg/l as soon as the wastewater is diluted with the algae and medium at day one after the process initiated, finally the COD was found to be at 1600mg/l at 9th day testing. As shown in above table 4 the removal efficiency of COD concentration in the treatment test is 33.33%. Further reduction was not able to take place because the ability of the algae to reduce and consume the nutrients was consumed completely at some stage after 10 days of continuous test, due to the high toxicity of the wastewater. It has been observed that the color of the algae got changed after 10 days of treatment, which refers or suggest that the algae has died in the declining stage of growth curve due to the unavailability of nutrients and food source.
To reduce the COD to further safety level of less than 100mg/l the wastewater has to be treated in the same way but with a bigger and open natural pond system and also to try with some different species of macro algae like Brown freshwater macro algae or red freshwater and sea water macro algae. Algae are good in taking nutrient rich chemicals like nitrogen and phosphorous as food source and sometimes converts them into carbohydrates and lipids. TOC in the real wastewater is found to be 1206 ppm for NPOC (Non-Purgeable Organic Carbon).

Here the crepe cotton wastewater is rich in nitrate and phosphate nutrient which are suitable in the growth of macro algae reducing its content from the wastewater and making the wastewater safe to discharge anywhere in pond or lake or agricultural fields, the initial N and P values of the wastewater is high which is been successfully consumed by the algae in the treatment process and the least water was free from N and P (almost free), as shown in Figure 2. The concentration of N and P in the real wastewater is 60.236mg/l and 19.132mg/l respectively, from the resultant table the concentration of these N and P have been very well reduced or consumed by algae in the process (Aslan & Kapdan, 2006)[6].

At final stage when the algae is at its declining phase, the concentration of N and P was reduced to 7.300mg/l and 4.800 mg/l respectively. The removal efficiency of N and P is 17.6% and 35.9% respectively, from the above result, we can say that macro algae are effectively taking Nitrogen and Phosphorous in the form of nutrient.

Ammonia is also a nutrient present in the crepe cotton wastewater, which needs to be reduced or removed before discharging the water(Gonzalez, Canizares, & Baena, 1997)[7].

**Figure 1:** Change in COD concentration during treatment

**Figure 2:** Change in concentration of N and P
As the result shows that initial ammonia is 4.110mg/l and as the treatment process progresses day by day reduction in the concentration level of ammonia is observed, 1.970mg/l after 9\textsuperscript{th} day of testing. As shown in the below figure 3. The removal efficiency of ammonia is 56.77%.

![Figure 3: Change in the concentration of ammonia](image)

Sulphate having a very little contribution in the concentration and toxicity of crepe cotton wastewater, the real wastewater having Sulphate concentration of 2.239mg/l. Every wastewater having some level of solids present in the form of TSS, TDS, TS, FS, their concentration in this crepe cotton wastewater is as follows, also the figure 4 and figure 5 shows about the effect of TSS and TDS respectively in the process. The presence of Total Suspended Solid in the crepe cotton wastewater is 58 mg/l which is not much high when compared to other toxic industrial wastewater, the visibility of the wastewater is dark thick or turbid, foam water type.

![Figure 4. Change in total suspended solids during treatment](image)

Concentration of TSS increases as the system treats the wastewater due to the mix of algae with wastewater, macro algae too contribute in the increment of TSS, because algae starts to break themselves in the mix and so the water which is to be discharged will be having more suspended solids. Fixed solids are found to be at average level in the real crepe cotton wastewater 252mg/l. Total solids are contributing well in the treatment process with 12600mg/l of total solids are present in the real wastewater. The presence of Total Dissolved Solids in the wastewater is 2480mg/l, which is initially got reduced (1180mg/l) after the dilution and as the days pass on, the algae are also getting dissolved in the wastewater treatment process and at one stage it reached to 1420mg/l.
Crepe cotton wastewater is highly alkaline both in phenolphthalein alkalinity and total alkalinity with 1147.5mg/l of phenolphthalein alkalinity and 3136.5mg/l of total alkalinity.

4. CONCLUSION

The concentration of COD, Nitrate, Ammonia, and Phosphate is getting reduced successfully by Macro algae. Observed that the aeration of wastewater (control) alone is not effective in reducing the COD, so it is necessary for the algae to be added. Also the oil and grease content present in the wastewater is evaporated and only the milk like thick white wastewater is remained, in this research macro algae are capable in reducing the concentration of COD of cotton processing wastewater.

With this, we can conclude saying that in natural pond system the result of decreasing rate of COD concentration in the wastewater will be more effective. Then it will be safe to discharge the water to any agricultural field or for gardening purpose. By increasing the quantity and quality of algae along with the conditions favoring like sunlight for photosynthesis, maintaining the pH at 8.0 and keeping the temperature below 35d Celsius. With these factors it has been observed that algae reduces the COD concentration and other chemical nutrients which are present in the wastewater, so algae will consume these chemicals and then the treated wastewater can be discharged to any agriculture field or can be drained into the nearby drainage system.

Algae provide an effective wastewater treatment. It helps to treat most of the industrial waste water thereby reducing the prevalence of diseases. This can help to preserve the fresh water resource. It contribute to better nutrient and food security for many household. The biofuel and ethanol production from algae is having much more attraction. Overall Production and cultivation of microalgae plays important role in biological application.

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