Biosorption of Thymol Blue in Waste Water using Activated Carbon of Cynodon Dactylon

1.Dr.V.Krishnasamy , 2.G.Mathubala

1. *Prof. & HOD of Chemistry , Bharath University,*
2. *Assistant Prof. of Chemistry , Bharath University,*

Abstract:

The presence of dye effluents in surface water is becoming a severe environmental and public health problem. Biosorption is potentially an attractive technology for treatment of wastewater for removing color constituents, heavy metal, etc., from industrial wastewater. Natural plant materials and agricultural wastes are applied in Biosorption technology to remove color constituents from aqueous media. They offer an efficient and cost-effective alternative to traditional chemical and physical remediation and decontamination techniques. In this project we use Cynodon dactylon (Arugampul) to remove Thymol blue.

Keywords: *Effluents, Biosorption , aqueous media , remediation, decontamination , Cynodon dactylon (Arugampul)*

1. INTRODUCTION

1.1. Wastewater:

Wastewater is any water that has been adversely affected in quality by anthropogenic influence. It comprises liquid waste discharged by domestic residences, commercial properties, industry, and/or agriculture and can encompass a wide range of potential contaminants and concentrations. In the most common usage, it refers to the municipal wastewater that contains a broad spectrum of contaminants resulting from the mixing of wastewaters from different sources.

Sewage is correctly the subset of wastewater that is contaminated with feces or urine, but is often used to mean any waste water. "Sewage" includes domestic, municipal, or industrial liquid waste products disposed of, usually via a pipe or sewer or similar structure, sometimes in a cesspool emptier.

The physical infrastructure, including pipes, pumps, screens, channels etc. used to convey sewage from its origin to the point of eventual treatment or disposal is termed sewerage.

1.2 Wastewater constituents:

The composition of wastewater varies widely. This is a partial list of what it may contain:

- Water (> 95%) which is often added during flushing to carry waste down a drain;
- Pathogens such as bacteria, viruses, prions and parasitic worms;
- Non-pathogenic bacteria;
- Organic particles such as feces, hairs, food, vomit, paper fibers, plant material, humus, etc.;
- Soluble organic material such as urea, fruit sugars, soluble proteins, drugs, pharmaceuticals, etc.;
- Inorganic particles such as sand, grit, metal particles, ceramics, etc.;
- Soluble inorganic material such as ammonia, road-salt, sea-salt, cyanide, hydrogen sulfide, thiocyanates, thiosulfates, etc.;
- Animals such as protozoa, insects, arthropods, small fish, etc.;
- Macro-solids such as sanitary napkins, nappies/diapers, condoms, needles, children's toys, dead animals or plants, etc.;
- Gases such as hydrogen sulfide, carbon dioxide, methane, etc.;
- Emulsions such as paints, adhesives, dyestuffs , mayonnaise, hair colorants, emulsified oils, etc.;
- Toxins such as pesticides, poisons, herbicides, etc.

1.3. Types of Wastewater

Wastewater is domestic, municipal, or industrial liquid waste products. Depending on their origin, wastewaters can be classed as sanitary, commercial, industrial, or surface runoff.

Sanitary sewage: The spent water from residences and institutions, carrying body wastes, ablution water, food preparation wastes, laundry wastes, and other waste products of normal living, are classed as domestic or sanitary sewage.

Commercial wastes: Liquid-carried wastes from stores and service establishments serving the immediate community, termed commercial wastes, are included in the sanitary or domestic sewage category if their characteristics are similar to household flows.

Surface runoff: It is also known as storm flow or overland flow, is that portion of precipitation that runs rapidly over the ground surface to a defined channel. Precipitation absorbs gases and particulates from the atmosphere, dissolves and leaches materials from vegetation and soil, suspends matter from the land, washes spills and debris from urban streets and highways, and carries all these pollutants as wastes in its flow to a collection point. Discharges are classified as point-source when they emanate from a pipe outfall, or non-point-source when they are diffused and come from agriculture or unchanneled urban land drainage runoff. Any sewage discharged from a vessel will be either one of the following two categories, (i) treated sewage or (ii) untreated sewage.

Treated sewage: It is sewage that has passed through an onboard sewage treatment system and has three distinct grades, that is, Grade A, Grade B and Grade C treated sewage. Grade C is the lowest level of treatment, Grade B is a higher level of treatment and Grade A is the highest level of treatment. Macerated sewage is not treated sewage.

Untreated sewage: It is all sewage that is not treated sewage - sewage that has not passed through a treatment system. This is sewage that is discharged directly from a toilet into a waterway (in areas where discharge is permitted) or contained in an onboard holding tank. Any untreated sewage that is discharged, in areas where the discharge of untreated sewage is permitted, must first pass through a macerator. Macerated sewage is untreated sewage.

1.4.wastewater treatment technologies:

- **Activated sludge method*:*** Activated sludge is a process for treating sewage and industrial wastewater using air and biological floc composed of bacteria and protozoans.
- **Anaerobic Digestion:** Anaerobic digestion is a series of processes in which microorganism breakdown biodegradable material in the absence of oxygen.
- **Sedimentation:** Sedimentation is the tendency for particles in suspension to settle out of the fluid in which they are entrained, and come to rest against a barrier. This is due to their motion through the fluid in response to the forces acting on them: these forces can be due to gravity, centrifugal acceleration or electromagnetism. In geology sedimentation is often used as the polar opposite of erosion, i.e., the terminal end of sediment transport. In that sense it includes the termination of transport by saltation or true bedload transport. Settling is the falling of suspended particles through the liquid, whereas sedimentation is the termination of the settling process.
- **Treatment pond**: A treatment pond treats water fouled by anaerobic bacteria. It is used mainly by tree nurseries, dairy farms and other agricultural companies near horse or cattle sheds or barns. The pond treats polluted stormwater and animal wastewater so that it may be returned to the environment as fertilizer and irrigation water.
- **Froth flotation**: Froth flotation is a process for selectively separating hydrophobic materials from hydrophilic. This is used in several processing industries. Historically this was first used in the mining industry.
- **Flocculation:** Flocculation, in the field of chemistry, is a process wherein colloids come out of suspension in the form of floc or flakes by the addition of a clarifying agent. The action differs from precipitation in that, prior to flocculation, colloids are merely suspended in a liquid and not actually dissolved in a solution. In the flocculated system, there is no formation of a cake, since all the flocs are in the suspension.

1.5. Waste Water Treatment by activated carbon:

Activated carbon is one of the most effective media for removing a wide range of contaminants from industrial and municipal waste waters, landfill leachate and contaminated ground. As the world's most powerful adsorbent, it can cope with a wide range of contaminants. Different contaminants may be present in the same discharge and carbon may be used to treat the total flow, or it may be better utilized to remove specific contaminants as part of a multistage approach.

The specification and quality of this material is tightly controlled, ensuring the customer receives a reliable product. With dedicated industrial tankers and mobile equipment, Chemviron Carbon, can provide an exceptional service that helps customers meet and exceed their environmental responsibilities.

The typical range of environmental water contaminants that activated carbon is used to treat includes:

- Non-biodegradable organic compounds (COD)
- Toxicity
- Colour compounds and dyestuffs
- Inhibitory compounds for biological treatment systems
- Chlorinated/halogenated organic compounds
- Pesticides

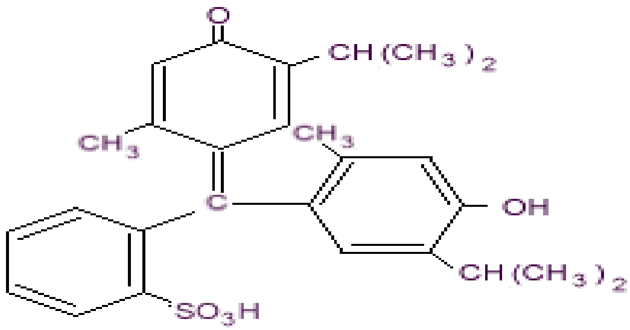
1.6.The benefits of this process include:

- Improved removal of Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), non-biodegradable organic compounds and toxicity
- Increased stability to shock loads
- Removal of inhibitory compounds including for nitrifying bacteria
- Improved sludge dewatering
- Reduced aerator foaming.

2. Thymol Blue:

Thymol blue (thymolsulphonephthalein) is a brownish-green or reddish-brown crystalline powder that is used as a pH indicator. It is insoluble in water but soluble in alcohol and dilute alkali solutions. It transitions from red to yellow at pH 1.2–2.8 and from yellow to blue at pH 8.0–9.6.

Structure:
Thymol Blue.



Properties(Table-1):

Chemical Formula	$C_{27}H_{30}O_5S$
Molecular Weight	466.60
Melting Point	221 - 224° c
Dye Content	~95%
Transition Range	pH 1.2 - 2.8 Red to Yellow pH 7.8 - 9.5 Yellow to Blue
Appearance	Brownish-green crystal powder
Solubility in water	Insoluble

2.1 Preparation of Thymol Blue solution**:**

A synthetic solution of Thymol Blue was prepared from analytical reagent grade Thymol Blue powder and stored in polythene bottles. The pH of the solution was adjusted to the required level, using HCL and NaOH solutions.

3.. Selection of Bio Material:

Figure-1: Arugampul (Cynodon dactylon)

3.1. The Taxonomic Status of the plant:

The Plant Cynodon dactylon Pers. is commonly known as Bermuda Grass, Cocksfoot-grass, Couch grass, Dog's tooth, European Bermuda Grass, Grama, Handjes grass and Stalian Ayrigi. It belongs to the family Gramineae (Poaceae). In Hindi language it is known as Doob and Durwa in Sanskrit.

3.3. Uses:

A valuable pasture and excellent fodder grass, staying green during hot weather. It can grow in very diverse conditions of soil and moisture, withstanding drought well and also tending to eliminate other plants. Provides more and better grazing for horses and cattle than any other grass; also used for hay and ensilage. The rhizomes are given to horses. It is also valuable for soil conservation due to its long runners that root at the nodes. It is difficult to eradicate and can become a serious weed in cultivated land. In many areas it is used for lawn and turf, and in Hawaii it is considered an excellent lawngrass.

3.4.Folk Medicine:

Bermudagrass is reported to be alterative, anecbolic, antiseptic, aperient, astringent, cyanogenetic, demulcent, depurative, diuretic, emollient, sudorific, and vulnerary (Duke and Wain, 1981); it is reported to be photosensitizing in animals, to cause contact dermatitis (Lewis and Elvin-Lewis, 1977), and hayfever (Degener, 1957-1963). It is a folk remedy for anasarca, calculus, cancer, carbuncles, convulsions, cough, cramps, cystitis, diarrhea, dropsy, dysentery, epilepsy, headache, hemorrhage, hypertension, hysteria, insanity, kidneys, laxative, measles, rubella, snakebite, sores, stones, tumors, urogenital disorders, warts, and wounds (Duke and Wain, 1981)[9],[10],[11].

3.5. Chemistry:

Per 100 g, the wet matter is reported to contain on a zero-moisture basis 11.6 g protein, 2.1 g fat, 75.9 g total carbohydrate, 25.9 g fiber, 10.4 g ash, 530 mg Ca, 220 mg P, 112.0 mg Fe, 1630 mg K, 28 ug beta-carotene equivalent (Miller, 1958). Bermudagrass is reported to contain cynodin, hydrocyanic acid, and triticin (Watt and Breyer-Brandwijk, 1962)[12],[13].

4. Preparation of Biocarbon:

Cynodon dactylon is an important ornamental Plant widely distributed in agricultural fields. The plant leaves were collected and air dried for 48 hours. The dried leaves were ground in ball mills and the screened homogeneous powder was used for the preparation of biocarbon. Activated biocarbon was prepared by treating the leaves powder with the concentrated sulphuric acid(Sp. Gr. 1.84) in a weight ratio of 1:1.8(biomaterial: acid). The resulting black product was kept in an air –free oven maintained at 160±5° c. The particle size of activated carbon between 90 and 125 micrometer was used.

4.1. Characterisation of the Activated Biocarbon:

The activated Biocarbon obtained from the Cynodon dactylon prepared by above method were taken for analyzing the following characteristics.

4.2. Apparent Density:

A 100 ml graduated cylinder was weighed accurately. Sufficient amount of carbon was transferred with constant taping and filled to the 50 ml mark. The shaking attached to the balance should be adjusted, so that the graduated cylinder was filled with carbon approximately 1 ml per second. After filling the graduated cylinder with the carbon, it was weighed. The apparent density was calculated by dividing the weight of the carbon by 50.

4.3. pH:

About 10 gram of the dried material was weighed and transferred into a 1000 ml beaker. 300ml of freshly boiled and cooled water was added (adjusted to pH 7) and heated to boil. Digested for 10 minutes and filtered while hot, rejecting the first 20 ml of the filtrate and the filtrate was cooled to room temperature and determined its pH Value.

4.4. Structural Investigation:

The following analytical methods were employed for the analysis of structure and morphological features of the biocarbon.

5.FT-IR analysis:

Fourier transform infrared spectrometry(Perkin-Elmer) was used analyze the organic functional groups in the adsorbent. The transmission spectrum was acquired at a 64 scans with 4 cm- 1 resolution and the spectrum was corrected for a KBr background.

5.1. Biosorption Process:

This is a single stage process involves removal of Thymol Blue from aqueous solution using biocarbon. The percent removal of Thymol Blue on the adsorbents was calculated from,

$$\% \text{ Removal} = \frac{C_o - C_f}{C_o} \times 100$$

Where, C_o is the initial concentration of Thymol Blue and C_f is the final concentration of Thymol Blue.

5.2. Adsorption Studies:

All experiments were conducted by Batch studies. The batch experiment was the basis of the experiment in which the adsorption process occurs. This method involves following steps.

5.2.1 Optimisation of carbon dosage:

Different weights of carbon ranging from 1.0-3.0 gram were weighed and made to contact with 100ml of 25ppm Thymol Blue solution for about 90 minutes. The amounts of Thymol Blue present in these solutions after treatment were determined by using the Colorimetric method.

5.2.2. Optimisation of contact time:

Optimized Dosage of carbon was weighed and made to contact with 100ml of 25ppm Thymol Blue solution and the amount of Thymol Blue present in the solution were determined at regular intervals of time(15 to 120 minutes) by above colorimetric method.

5.2.3 Optimisation of pH:

Optimized Dosage of carbon was weighed accurately and made to contact with 100ml of 25ppm Thymol Blue solutions of pH 1 to 7 for Optimized Time Duration. The solutions were filtered and the amount of Thymol Blue in these solution were determined by colorimetrically.

6. RESULT AND DISCUSSION

The carbon derived from Cynodon dactylon was characterized to find the suitability for the removal of color and other pollutants from wastewater. Apparent Density and pH are some of the characteristics which were determined. In all these case carbon of 40-50 mesh size was used.

6.1 Characterisation:

6.1.1 Apparent Density:

The apparent density of the carbon was found to be 0.36 g/ml. Apparent density may be regarded as a measure of activity of the carbon and the carbon is in contact with water leaking of impurities from carbon should not be significant so that the desired quantity of the effluent is not altered.

6.1.2 pH:

The pH of the carbon was found to be 2.22. The pH of carbon is due to mostly the inorganic ingredients present in the source material and the actual value of pH will be determined by conditions under which the carbon was prepared and subjected to use.

6.2 Structural investigation:

6.2.1.FT-IR analysis:

The IR absorption spectra of the Cynodon dactylon plant leaves biocarbon is shown in Figure 2.1. The IR spectra of the biocarbon proved that the Amide and Amine Group (3170 cm^{-1} and 1606 cm^{-1}) contained in the structure of the biocarbon.

The FT-IR spectrum of biocarbon after treatment with the wastewater containing Thymol Blue is shown in Figure 2.2. The IR spectra of the biocarbon after treatment the wastewater containing Thymol Blue dye molecules show similar absorption bands with the presence of Phenolic –OH(3399 cm^{-1}) functional group, which responsible for their adsorption characteristics. Although both biocarbon showed great similarities in their surface area, the presence of similar chemical groups on their surfaces could result in almost similar adsorption behavior.

Figure 2.1 FT-IR spectrum of biocarbon

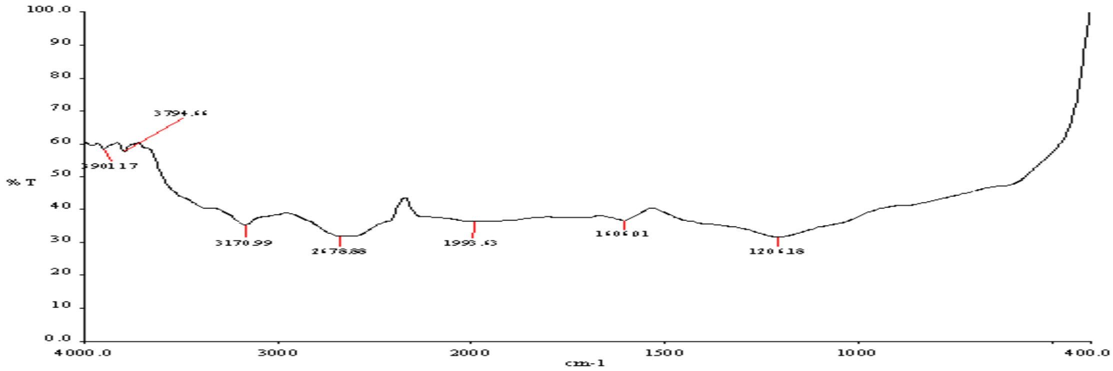
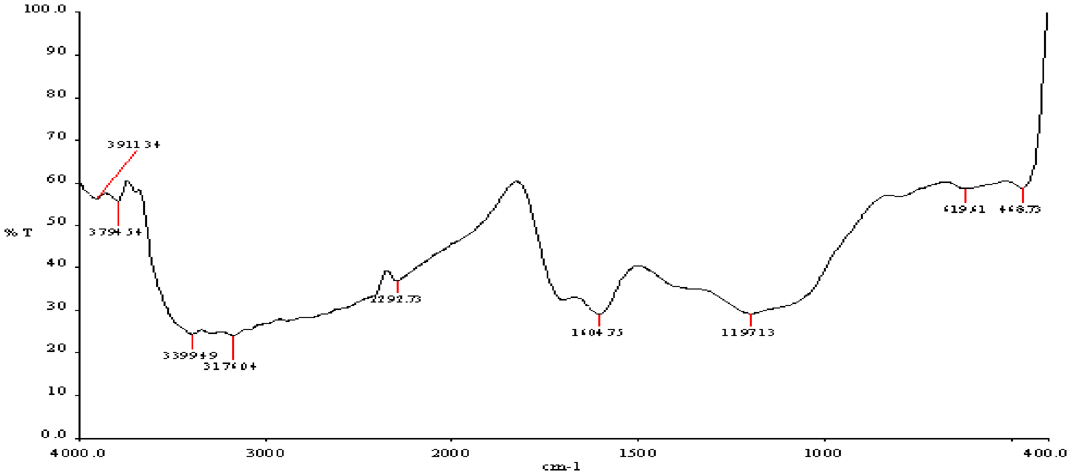


Figure 2.2 FT-IR spectrum of biocarbon after biosorption process.



6.3 Adsorption studies:

Batch experiments were conducted with standard solution of congo red and the results are furnished in the following pages.

6.3.1 Effect of Carbon Dosage:

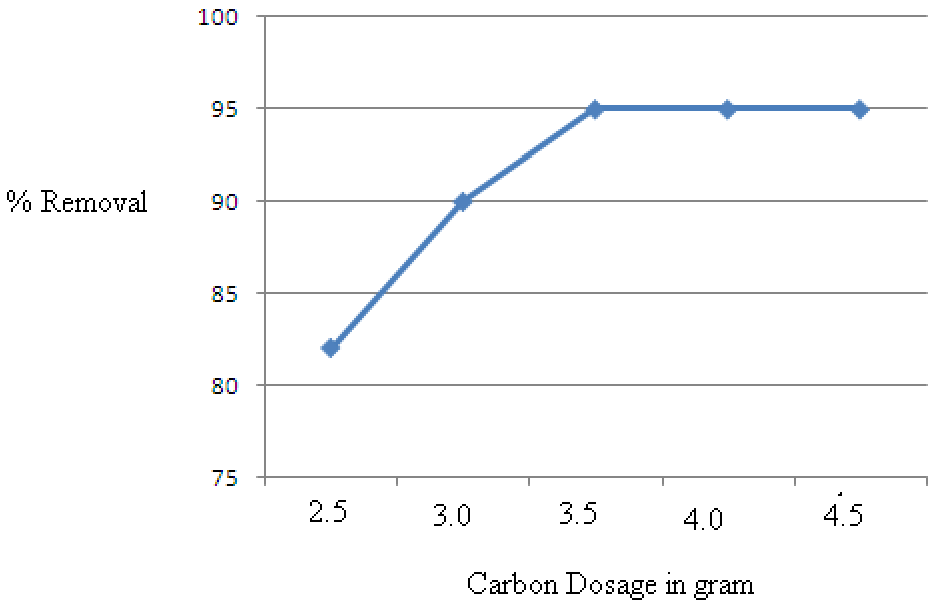
The adsorption of Thymol Blue on the activated carbon was found to increase with the increasing amount of carbon.(Figure 3.1). This is mainly due to the increase in the total area of the adsorbent. The amount of adsorbent for 95% removal of Thymol Blue was 3.5g/100ml.

Table-2:
Effect of Carbon Dosage for Thymol Blue Removal:

Concentration of Thymol Blue solution : 25 ppm
Contact time : 120 mins.

S.No	Carbon Dosage (gram)	% Removal
1	1.5	60
2	2.0	70
3	2.5	82
4	3.0	90
5	3.5	95
6	4.0	95
7	4.5	95

Figure 3.1: Effect of Carbon Dosage



6.3.2 Effect of Contact Time:

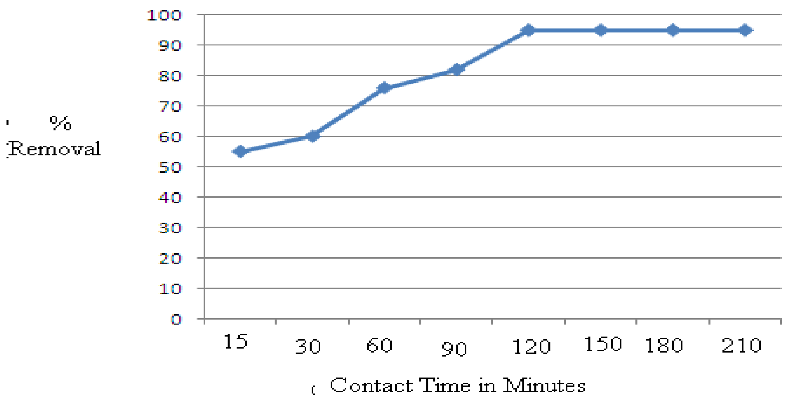
The effect of contact time on the percentage removal of Thymol Blue from water is given in Figure 3.2. The optimum contact time was found to be 120 minutes. It was observed that the uptake of Thymol Blue on the activated biocarbon was not very rapid but remains constant after 120 minutes.

Table-3:
Effect of Contact Time for Thymol Blue Removal:

Concentration of Thymol Blue solution : 25ppm
Optimum carbon dosage : 3.5 gram

S.No	Contact Time (minutes)	% Removal
1	15	55
2	30	60
3	60	76
4	90	82
5	120	95
6	150	95
7	180	95
8	210	95

Figure 3.2: Effect of Contact Time



6.3.3 Effect of pH:

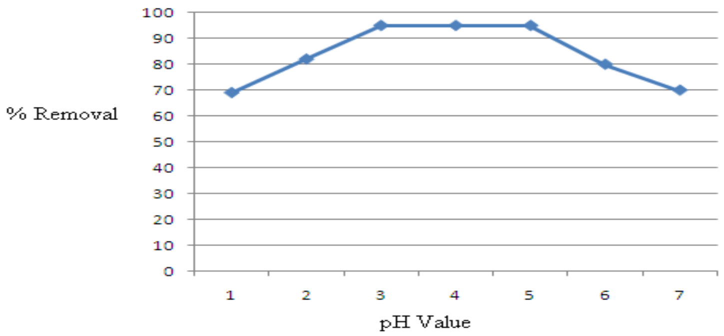
The adsorption of Thymol Blue on the carbon at various pH levels is given in figure 3.3. Thymol Blue was found to be adsorbed in a pH of 3 to 5. Adsorption decreases below pH 3 and above pH 5.

Table-4:
Effect of pH for Thymol Blue Removal:

Concentration of Thymol Blue solution : 25 ppm
Contact time : 120 mins.
Optimum carbon dosage : 3.5 gram

S.No	pH	% Removal
1	1	69
2	2	82
3	3	95
4	4	95
5	5	95
6	6	80
7	7	70

Figure 3.3: Effect of pH



7. CONCLUSION

The presence of dye effluents in surface water is becoming a severe environmental and public health problem. These are often discharged from number of industries and dying factories which can contaminate the freshwater and marine water.

Biosorption is potentially an attractive technology for treatment of wastewater for removing color constituents from industrial wastewater. Natural plant materials and agricultural wastes are applied in biosorption technology to remove color constituents from aqueous media. They offer an efficient and cost-effective alternative to traditional chemical and physical remediation and decontamination techniques.

In the present research work, the following conclusions can be made.

* The efficiency of the biocarbon is excellent.

* The percentage removal of Thymol Blue in the synthetic wastewater system was 95% with the effective biocarbon load of 3.5 gram/ 100ml of the sample.

* The handling of the biomaterial is very easy and harmless.

* The experimental conditions are very simple and operational cost is low.

* The proposed bioremediation technology is economically feasible and eco-friendly in nature.

* The method can be recommended for the color removal of high concentration of Thymol Blue from industrial wastewater.

* This process can be effectively used for the color removal of Thymol Blue and other heavy metal from industrial wastewater.

Preliminary treatment of the industrial wastewater is essential before applying this methodology.

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