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Biosorption of Thymol Blue from Industrial Wastewater Using Activated Biocarbon from *Cynodon dactylon* Plant Leaves

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Abstract: The objective of this study was to evaluate the performance of the activated biocarbon under optimum experimental conditions to be used in water treatment. A synthetic solution of Thymol Blue was prepared. Activated carbon is one of the most effective media for removing a wide range of contaminants from industrial and municipal waste waters and contaminated ground. 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. This process can be effectively used for the color removal of Thymol Blue and other heavy metal from industrial wastewater.
Keywords: activated biocarbon, Thymol Blue, contaminated, Cynodon dactylon, pollutants.

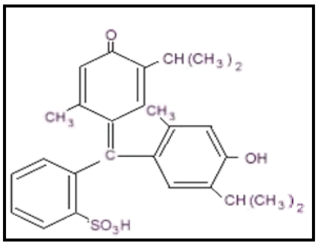
Introduction

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., 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[1-4].

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. The benefit of this process includes improved removal of Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), non-biodegradable organic compounds and toxicity.

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[5, 6].

Thymol Blue.



Properties(Table-2)

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

Contamination of drinking water supplies from industrial waste is a result of various types of industrial processes and disposal practices. Industries that use large amounts of water for processing have the potential to pollute waterways through the discharge of their waste into streams and rivers, or by run-off and seepage of stored wastes into nearby water sources. Other disposal practices which cause water contamination include deep well injection and improper disposal of wastes in surface impoundments.

Industrial waste consists of both organic and inorganic substances. Organic wastes include pesticide residues, solvents and cleaning fluids, dissolved residue from fruit and vegetables, and lignin from pulp and paper to name a few. Effluents can also contain inorganic wastes such as brine salts and metals. The Clean Water Act has standards for the permitted release of a limited amount of contaminants into waterways. This is an incentive for industry to pre-treat their water by neutralizing the chemically active components, recycling, dilution or extraction and collection for proper disposal[7]. More than 200,000 sources of waste water are regulated by the National Pollutant Discharge Elimination System (NPDES) permit program.

The levels of contaminants in drinking water are seldom high enough to cause acute (immediate) health effects. Examples of acute health effects are nausea, lung irritation, skin rash, vomiting, dizziness, and even death. Contaminants are more likely to cause chronic health effects - effects that occur long after repeated exposure to small amounts of a chemical. Examples of chronic health effects include cancer, liver and kidney damage, disorders of the nervous system, damage to the immune system, and birth defects[8].

Materials and Methods

Preparation of Synthetic Wastewater

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.

Selection of Bio Material

Figure-1: Arugampul(Cynodon dactylon)

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.

In view of environmental significances, the Biosorption of Thymol Blue on the activated biocarbon has been investigated under different experimental conditions. The objective of this study was to evaluated the performance of the activated biocarbon under optimum experimental conditions to be used in water treatment. To evaluate various operating parameters such as effect of pH, Contact time, Biosorption does for the biocarbon produced from plant leaves. To study the effect of chemical activation on the development of pore structure on the biocarbon produced. To examine the characteristic of granular biocarbon produced i.e., Biosorption capacity and surface functionality of the biocarbon produced. To evaluate the potential application of locally produced biocarbon in industrial wastewater for color removal process.

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)[9-11].

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].

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 $160\pm5^{\circ}$ c. The particle size of activated carbon between 90 and 125 micrometer was used.

Characterisation of the Activated Biocarbon

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

Structural Investigation

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

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.

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.

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.

Optimisation of carbon dosage, contact time and pH

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. 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. 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 solutions was determined by colorimetrically.

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.

Characterisation

Structural investigation

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.

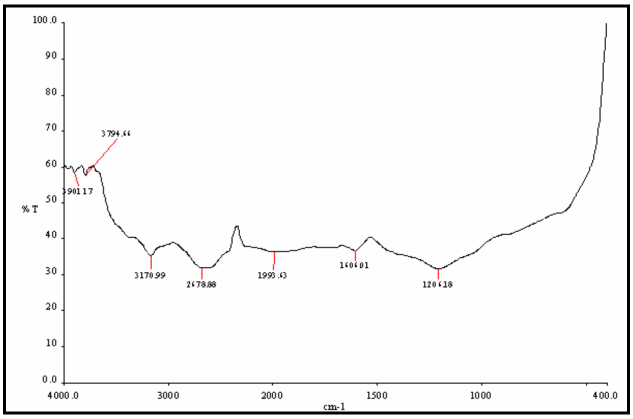


Figure 2.1 FT-IR spectrum of biocarbon

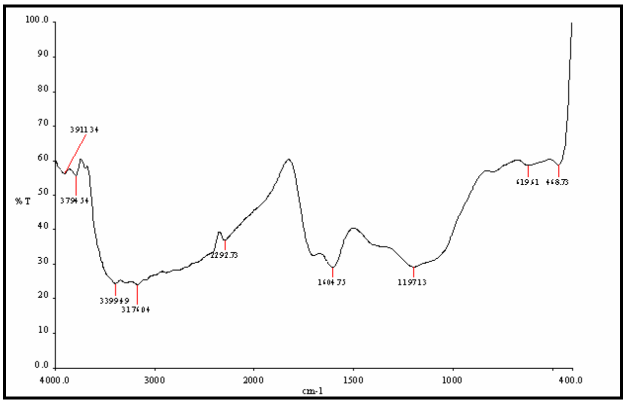


Figure 2.2 FT-IR spectrum of biocarbon after biosorption process.

Adsorption studies

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

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-3: 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

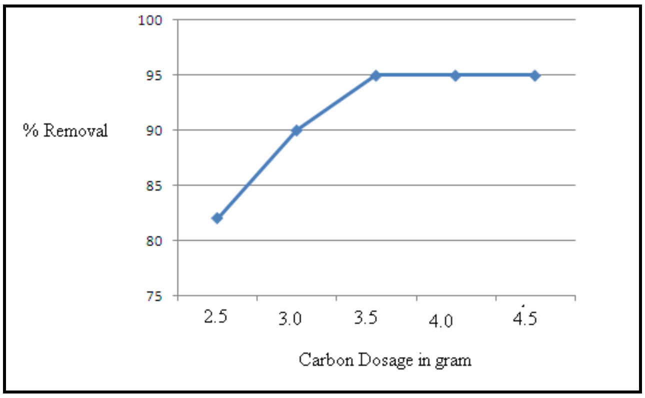


Figure 3.1: Effect of Carbon Dosage

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-4: 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

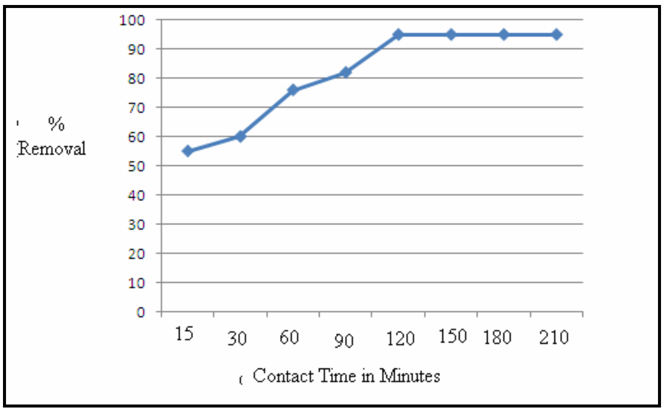


Figure 3.2: Effect of Contact Time

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-5: 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

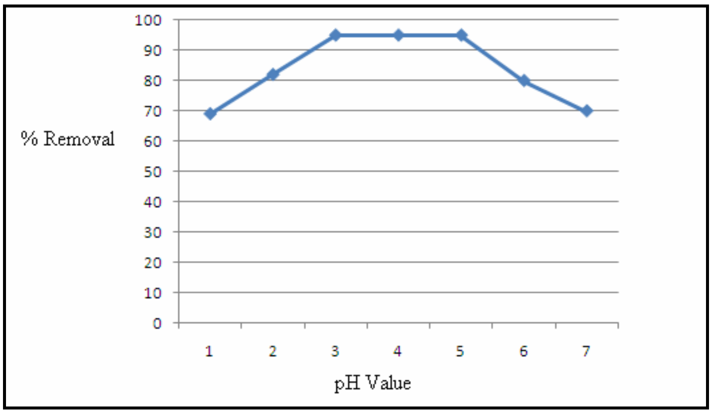


Figure 3.3: Effect of pH

Summary and 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 and 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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