DECLOURIZATION OF DYE EFFLUENT (SPECIFICALLY MALACHITE GREEN DYE) FROM TEXTILE INDUSTRIES BY COMBINATION OF PHYSICOCHEMICAL AND BIOLOGICAL METHODS

Dr. Avnish Sharma
Assistant Professor
Department of Chemistry
MLV Government College, Bhilwara (Raj)

Abstract

Dye or a dyestuff is usually a coloured organic compound or mixture that may be used for imparting colour to a substrate such as cloth, paper, plastic or leather in a reasonably permanent fashion. Previously dyes were obtained from animal and vegetable sources. Today most of the available dyes are synthetic dyes, prepared from aromatic compounds which are obtained from coaltar or petroleum.

As Bhilwara (Rajasthan) is a hub of Textile industry Nevertheless, it produces about 75 % of the country's textile. However, there is a dark side to its gloss. The enterprise's bad effluent control system has long-lasting poisoned the area's groundwater affecting agricultural lands and people's fitness. The pollution maintains unabated even after pollution manage government set a 0-discharge norm for the units. Experts fear it will soon reach the city's centre and poison groundwater meant for domestic purposes.

Always the Textile industry involves processing or converting raw material/fabric into finished cloth/material employing various processes/operations and consumes large quantities of water and produces extremely polluting waste effluents [1].

It consumes large quantities of water for various processes and discharge equally large volumes of wastewater containing a variety of pollutants. It is estimated that 10-70 liters of water may be required for processing one meter of cloth.

Waste Generation From Textile Industries

Characteristics of wastewater:- The water demand of industrial sector in the country has increased at a fast pace during the recent years, more particularly after implementation of liberalized policies for industrial development. Among the important water consuming industries, the textile industry ranks at the first place [2].

Among the leading textile printing centers in the country, Rajasthan state owns many, more particularly in the area of traditional printing. The important centers having large concentration, of textile printing industries in the state are BHILWARA, PALI, BALOTRA, BAGRU AND SANGANER.. These industries have been recognized as the most polluting industries in Rajasthan by the Central Pollution Control Board, New Delhi, as they discharge untreated effluents in the watercourses as well as the land forming pools of wastewater is a serious threat to the environment.

The dyes are the most visible pollutant in the wastewater. About 3500 dyes are in practical use. Azo dyes contribute 85% of which sulphonated azo dyes predominate. About 10-15% (128 ton/day globally) of dyes are lost at various finishing steps of the printed cloths [3].

A typical textile unit is expected to generate various type of wastewater, differing in magnitude and quality vis-à-vis environmental parameters. This is due to the variety of processes involved in textile industry. The entire wastewater generated in a composite textile mill originate from combination of the various operations detailed given in table below: -

In the current study, a physico-chemical approach along with a biological procedure were used to remove colour from the effluent of printing and dyeing businesses in the Bhilwara city of Rajasthan, specifically from the target dye Malachite Green Dye.

Introduction

Demographic and Industrial Position of Bhilwara:-

Demographically according to 2001 census Bhilwara city has a population of 280,128 on an area of 118.49 sq. km., extending between Sanganer and Pur, exhibits urban density of 2364 persons per sq. km., accounting for 13.9% of total population of the district. Bhilwara grew from 10346persons in 1901 to 29668 in 1951 and 280,128 in 2001. Bhilwara growth from 1951 onwards has been due to immigration, seeking employment, performing business activities and redefining of the municipal limit by merging Pur, Sanganer and other villages during 1961-1971 inter- censual period.

Bhilwara district is rich in agricultural and livestock resources for the industrial development of the city from where it is fed. Mewar Textile Mills was established in 1938 in Bhilwara which was the forerunner of textile industry. Synthetic textile units came into existence in late 1960s which have now spread over the world map of textile industry. There are more than 423,280 spindles in the district upto 2007 and Rs. 5000 crore worth production is being made by spinning and weaving units in Bhilwara. 25000 labourers are engaged directly or indirectly with the textile industry here.

As we see above Bhilwara is a fast developing city of the Rajasthan in both ways as Population and of industrial point of view and they both demanding water as most important essential thing. According to Mewar Chamber of Commerce and Industry (mcci) data, the 500 units require 24.80 million litres of water per day (mld).The 20 processing units use 80 per cent of this (19.34 mld).

Problem in general: -

Dyes which is a well-known synthetic organic product, is used by a wide number of industries. The colour is one such pollutant generally associated with water and wastewater in various forms. Bhilwara is one such example where unabated and indiscriminate discharge of coloured effluents from dyeing and printing has posed a serious pollution problem of multi-facet dimension. The textile printing and dyeing industry of this town, the pride of our state, is adding to our state income by leaps and bounds at one hand and at the same time, it is shame to see the ugly sights of effluent disposal on the other hand, It is not this simple disgrace, we feel sorry about, but the potential pollution hazards this industry is going to create in the near future.

The release of such compounds into the environment as a result of inadequate treatment could be detrimental to the natural ecosystem and human health due to potential toxic, mutagenic carcinogenic and/or bio accumulative effects. The land, the air and the water-three basic parameter ascertaining the health of environment are polluted with number of pollutants.

The textile wastewater are extremely diverse, and perhaps one of the most potential polluters of our aquatic environment. Textile processing effluents, when discharged into the receiving body of water without adequate treatment, affect the multi segments of the environment leading to irreversible persistent changes.

The high temperature effluents, when discharges into the receiving water body, increases its temperature, thus reducing the solubility of oxygen in the water, and induces septic and unfavorable conditions for survival of aquatic ecosystem. The highly alkaline nature of the effluents also has adverse effects on the aquatic ecosystem.

The solids will increase the turbidity of water, induce septic conditions in the water body by retarding the photosynthetic activity affecting the symbiotic process, and also interfere with oxygen transfer mechanism of air-water interface. The organic matter like starch, dextrin, and inorganic chemicals like sulfides, hydrosulpides, and nitrites will exerts an immediate oxygen demand, thus reducing the dissolved oxygen in water which will affect aquatic ecosystem.

Solution of the Problem: -

The only workable approach, given the severity of the contamination risks, is the total treatment of wastewater. Although in developing countries the cost of treatment has always been a crucial consideration when developing or implementing pollution control systems. To remove the colour from dye wastewater, there are several methods that can be used, including physical processes, chemical, physico-chemical processes, biological processes, etc.

The Present Study

For human ecologists, the waste from the dye business, which is high in both quantity and concentration, poses an even bigger challenge. Due to the significant concentration of textile businesses in Bhilwara, a tiny city, the study problem's origin is the same. There are around 20 well-known process houses operating here, including BSL, SUZUKI, SANGAM, and others, where the dying processes utilise a lot of water. In the present work physico-chemical method combined with biological process for removing the colour from the effluent of dyeing and printing houses of Bhilwara district. The specific objective of the present work is: -

(a) selecting sample dye based on their industrial uses

(b) beginning of the biological process

(c) Combined adsorption process

(d) Data interpretation and analysis

Colour Removal By Physico-Chemical Processes: -

Various physico-chemical processes like coagulation, flocculation, adsorption, ion exchange, reverse-osmosis and electrochemical coagulation have been investigated for treatment of coloured effluents.

In the present study the method which is used is **ADSORPTION** on different adsorption medium. Adsorption process is a sludge free-operation and produce high quality of treated effluent. Initially, activated carbon, prepared from various materials like coal, charcoal, wood, coke etc. has been used as sorbent and found to be highly efficient. Activated carbon has demonstrated its potential in removing colour from textile dye effluents [4,5,6,]. Activated carbon is effective for removal of the organic substances of relative low solubility because it provides a large interfacial area (surface) at which such substances may accumulate. A number of biological adsorbents have also been investigated for the removal of reactive dyes, these include apple pomace, wheat straw comcob and barley husk, maizecob, wood and rice hull etc (robinson, etal., 2002 and low and lee, 1997).

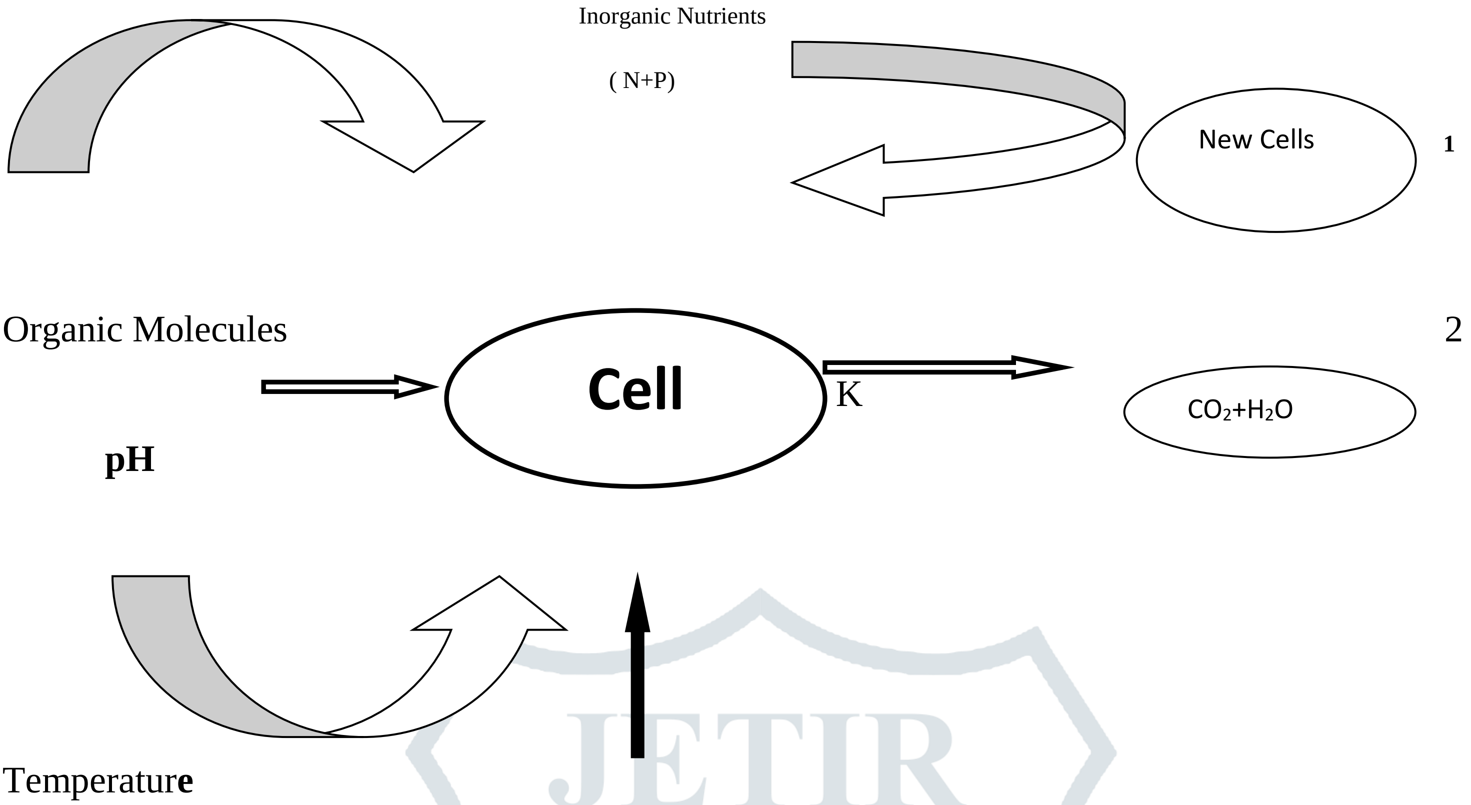
Though activated carbon demonstrates its potentiality in removing the textile effluent colour, but few disadvantages are also associated with this as high initial cost of carbon problems associated with regeneration/reuse facilities etc.[7].

PRINCIPLE OF ADSORPTION AND BIO-DEGRADATION

The use of low-cost adsorbent has been investigated as a replacement for the current expensive methods of removing dyes from waste water. The adsorbent use in present study are ***Treated Sugar Cane Bagasse and Azadirachta indica (NEEM) leaf power***

The colour in the effluent is mainly due to unfixed dye. The concentration of dye found in the effluent of textile industries depends upon the nature of dyes and dying process underway at the time (McMullan, *et al*., 2001). Lack in efficiency of dying process results in 15-30 % of all dye stuffs being lost directly to the wastewater (Perineau, *et al*., 1982). Even though they only make up a small part of the total amount of wastewater released following the dyeing process, textile dyes give it a highly coloured appearance (McKay, et al., 1985). An major issue is still how to remove dye economically. The removal of dye from wastewater has been the subject of much research (Perineau et al., 1982; McKay et al., 1985; Gupta, 1985; Khattri, 2000; Low et al., 2000; Liversidge, *et al*., 1997; Choy, *et al*., 1999, Asilian, *et al*., 2006).

Absorption studies were carried out for different temperature, pH’s and adsorbent doses.



BIODEGRADATION PROCESS

PRINCIPLE OF BIOLOGICAL DEGRADATION

Biological degradation or simply biodegradation is generally considered as a phenomenon of biological transformation of organic compounds by living organisms, particularly microbes. The role of micro-organisms in the decomposition of sewage and other organic wastes is long known.

It has been considered as a natural process in the microbial world as they use carbon as energy source for their growth and takes a pivotal role in the recycling of materials in the natural ecosystem. It brings about changes in the molecular structure of a compound ultimately yielding simpler and comparatively harmless (non-toxic) products like carbon dioxide, water, methane etc.

Biological treatment is a "natural process", organic matter in water will naturally decay as a result of the presence of microorganisms in receiving bodies of water. High organic loads in a wastewater will upset the businesses of receiving bodies of water and cause other undesirable effects. Biological treatment is engineered to accelerate natural decay processes and neutralize the waste before it is finally discharged to receiving water. This has helped microbes to act as scavengers and reduce the pollution load natural ecosystem.

Methodologies: -

This chapter deals with the various experimental methodologies adopted in this study together with a description of the materials: -

ADSORPTION TECHANIQUE:-

Dye solution preparation: - Dye solution prepared by weighing accurate quantity and dissolved in double distilled water to prepared stock solution (500 mg/L). Experimental solution of the desired concentration was obtained by successively dilutions. Dye concentration was determined by using absorbance values measured before and after the treatment by shimadzu UV spectrophotometer. Experiment were carried out at initial pH values ranging from 2 to 9, initial pH was controlled by the addition of NaOH (Sodium Hydroxide) or HCL (Hydrochloric Acid).

Adsorption experiment:

Preparation of adsorbent –

1. Treated sugar cane bagasse: - For this purpose the bagasse obtained from the site was dried under the open sky and sunlight until all the humidity evaporated and was then ground to fine powder. This ground bagasse was then sieved between -80 to +230 sizes. After this these ground bagasse then was treated with 2% formaldehyde for 5 hours. Then this bagasse filtered, washed with distilled water to removing formaldehyde and activated at 80^0C in the oven for 24 hours and kept in airtight container for further experiment.
2. Azadirachta Indica (Neem Leaves) -: Mature leaves of the Neem tree (Azadirachta Indica) was used after fine drying and grinding. It can also be used for adsorption of heavy metal ions from water [8].

Method employed :-

The method employed was very simple and effective. All adsorption experiments were carried out in batch processes. In each experiment 25 ml of the dye solution was mixed with 1gm of adsorbent in a 100 ml round bottom flask at room temperature (25 ± 1^0C) and (mixture was stirred on a rotator shaker) left to stand for prefixed time(. After predetermined time interval the mixture was filtered and the quantity of dye not adsorbed that is the dye remain in solution, was measured using a shimandzu UV-Vis, spectrophotometer.

Biological Treatment:-

Generally mixed cultures are more useful in degradation due to the large variety of micro-organisms which are capable of utilizing a multitude of metabolic intermediates (end product of biodegradation by one species may act as the substrate for another species and so on.)

Sludge collected from bhilwara dairy was used separately as seed to develop the culture for the biodegradation experiments. The diluted sludge was plated on to nutrient agar and the growth obtained after 24 hours, scraped, washed (4-5 times) with distilled water and used as the inoculums for the batch reactors.

Determination of COD (Chemical Oxidation Demand), Colorimetric Method: -

The chemical oxidation demand is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. The dichromate reflux method is preferred over procedures using other oxidants because of superior oxidizing ability, applicability to wide variety of samples. A sample is refluxed in strongly acid solution with a known excess of potassium dichromate ($K_2Cr_2O_7$). Colorimetric reaction vessels are sealed glass ampules. Oxygen consumed is measured against standards at 600 nm with spectrophotometer.

A. Reagents :

(a) Digestion solution : Add to about 500 ml distilled water, 10.216 gm ($K_2Cr_2O_7$), primary standard grade, previously dried at 100^0 C for 2 hours, 167 ml. Concentrate H_2SO_4 and 33.69 gm. $HgSO_4$ dissolve, cool to room temperature , and dilute to 1000ml.

(b) Sulphuric acid reagent: Add Ag_2SO_4 reagent to con. H_2SO_4 at the rate of 5.5 gm. Ag_2SO_4/Kg H_2SO_4. Let stand for 1-2 day to dissolve Ag_2SO_4.

(c) Potassium hydrogen phthalate standard : Lightly crush and then dry potassium hydrogen phthalate to constant weight to 120^0C. Dissolve 425 mg in distilled water and dilute to 1000ml. Potassium hydrogen phthalate (KHP) has a theoretical COD of 1.176 mg O_2/mg and this solution has a theoretical COD of 500 mg O_2/l this solution is stable when refrigerated for up to 3 months in the absence of visible biological growth.

B. Procedure:

Measure suitable volume of sample and reagents into tube or ampule as given in table below: -

Digestion vessel	Volume (ml) Sample	Volume (ml) Digestion solution	Volume (ml) Sulphuric acid reagent	Total final volume (ml)
Culture tubes 16 x 100 mm	2.5	1.5	3.5	7.5
20x150 mm	5.0	3.0	7.0	15.0
25x150 mm	10.0	6.0	14.0	30.0
Standard 10 ml ampules	2.5	1.5	3.5	7.5

Wash culture tubes and caps with 20% H_2SO_4 before first use to prevent contamination. Place sample in culture tubes or ampules and add digestion solution. Carefully run sulphuric acid reagent down inside of vessel so an acid later is formed under the sample digestion solution layer. Tightly cap tubes or seals ampules and invert each several times to mix completely and reflux for 2 hours at 150^0C and then cool to room temperature.

Invert cooled samples, blank and standards several times and allow solids to settle before measuring absorbance. Dislodge solids that adhere to container wall by gentle tapping and settling. Then pore these samples into quartz cuvette and place it into light path of UV-VIS spectrophotometer set at 600 nm. Read absorbance and compare to calibration curve and find out the COD of unknown samples.

Estimation of Residual Dye Concentration :-

Absorptionmetric measurements have been commonly employed for the investigation of concentration of coloured substances in the solution. Such studies have gained popularity due to simplicity and versatility of light absorption measurements. Such measurements are termed as spectrophotometric or absorptiometric.

In the spectrophotometric measurements, it is possible to employ almost all types of monochromatic light of a very narrow bandwidth by the dispersion of light through a prism or a grating. This fact is of great importance for precise measurement of absorbance, since the Beer-Lambert's law, holds good only with monochromatic radiations.

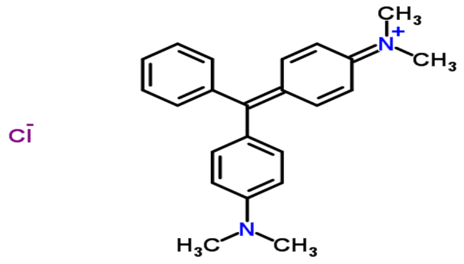
The Material (Dye) :-

Three dyes used for the present study purchased in pure form.

Malachite Green dye:

(a) Common name- Basic green 4/ Victoria Green B

(b) Formula -



(c) Compact Formula:-

$C_{23}H_{24}N_2$. HCl

(C23H25N2)2 (C2H2O4)3- Oxalate Salt

(d) Colour Index No. – 42000

(e) Molecular Weight

Hydrochloride salt = 364.9

Oxalate salt= 929

(f) Solvent – Water

(g) Group- Basic dyes

RESULT AND DISCUSSION

This chapter presents the detailed results of the several batch experiments using aqueous solution of selected dyes, which are generally regarded to be with limited water solubility and negligible volatility besides having wide industrial uses.

ADSORPTION STUDY:-

In each experiment(for pH effect) 25 ml of the dye solution was mixed with 0.5 gm of adsorbent in a 100 ml round bottom flask at room temperature (25 ± 1^0C) and (mixture was stirred on a rotator shaker) left to stand for prefixed time(. After predetermined time interval the mixture was filtered and the quantity of dye not adsorbed that is the dye remain in solution, was measured using a shimandzu UV-Vis, spectrophotometer.

The experiment was done by varying the amount of absorbents 0.1 to 1.0 mg 100 ml^{-}, concentration of the dye solution from 25 to 250 mg L^{-} (by diluting the stock solution) and pH at different time intervals.

Malachite Green dye :-

Adsorbents: (A.) Treated sugar cane bagasse (B.) Azadirachta Indica (Neem Leaves)

Contents: - 1. Effect of initial adsorbent dose 2. Effect of initial concentration of dye 3. Effect of pH

Table 1. Effect of the initial adsorbent dose (g/100ml^{-}) on dye removal, initial pH 6.5, concentration of dye=100mg L^{-}

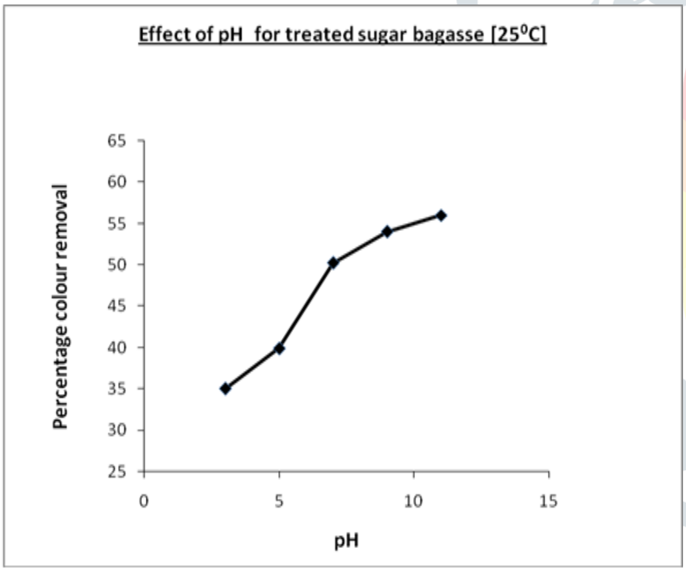
Initial adsorbent dose (g/100mL^{-})	Observed percentage of removal of colour with time (min)					
	10	30	50	70	90	110
Treated sugar cane bagasse						
0.1	7.5	9.3	13.20	16.45	18.50	22.00
0.3	19.30	21.35	24.25	33.25	37.55	43.60
0.5	33.25	37.22	40.25	42.35	52.25	59.25
0.7	37.25	41.25	45.00	52.00	58.25	62.00
1.0	40.50	45.25	49.90	54.25	58.25	63.50
Azadirachta Indica (Neem Leaves)						
0.1	8.25	10.22	12.00	14.50	20.00	22.25
0.3	19.25	24.00	29.25	32.50	37.00	44.25
0.5	30.25	36.25	40.40	46.25	53.65	59.00
0.7	35.00	40.25	48.66	55.25	59.60	69.50
1.0	40.25	43.50	51.50	58.35	62.25	73.50

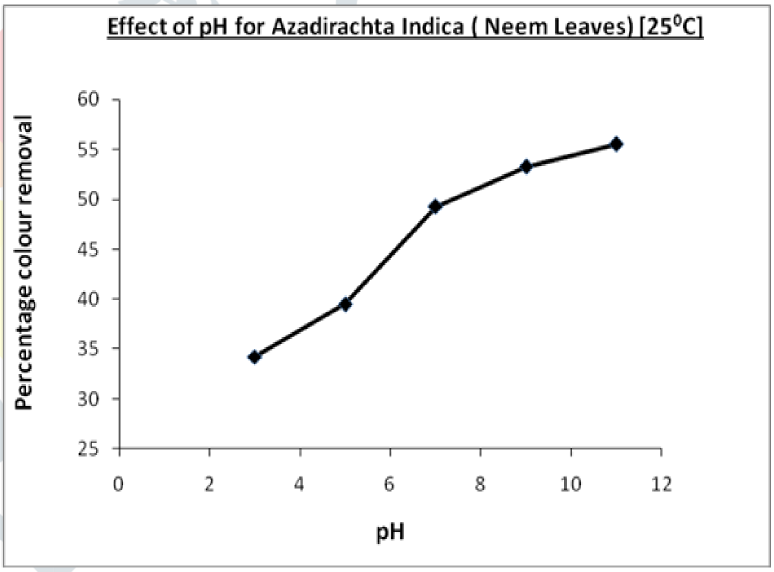
Table 2. Effect of the initial concentration of dye (mgL^{-}) on dye removal, initial pH 6.5, Adsorbent dose =0.5 g /100mL^{-}

Initial dye concentration mg L^{-}	Observed percentage of removal of colour with time (min)					
	10	30	50	70	90	110
Treated sugar cane bagasse						
25	70.25	75.25	78.60	82.55	87.25	90.00
75	55.25	64.50	68.25	72.30	75.25	85.00
125	30.00	39.00	44.00	45.00	53.25	63.25
200	26.20	30.25	35.55	40.50	48.25	52.00
250	20.00	24.00	33.25	38.00	45.00	50.00
Azadirachta Indica (Neem Leaves)						
25	73.00	78.25	82.00	85.25	87.25	90.50
75	50.00	55.25	60.25	68.10	70.00	78.50
125	28.20	34.20	37.00	44.50	50.20	56.50
200	24.20	28.50	36.00	40.20	45.00	49.00
250	20.00	24.50	30.00	38.20	40.00	44.25

Table 3. Effect of the pH on adsorption (Adsorbent dose =0.5 g /100mL) and initial dye concentration =100mg L$^-$, contact time 90 min, temperature =25^{0}C

Effect of pH for Treated sugar cane bagasse		
S.No	**pH values (-log H^+)**	**Observed percentage of removal of colour**
1.	**3**	**35.00**
2.	**5**	**39.90**
3.	**7**	**50.25**
4.	**9**	**54.00**
5.	**11**	**56.00**
Effect of the pH for Azadirachta Indica (Neem Leaves)		
1.	**3**	**34.25**
2.	**5**	**39.50**
3.	**7**	**49.25**
4.	**9**	**53.25**
5.	**11**	**55.50**





Graph No. 1. Effect of pH for treated sugar bagasse at 25^{0}C for Malachite Green dye

Graph No. 2. Effect of pH for Azadirachta Indica at 25^{0}C for Malachite Green dye

In this experiment, a pH of 5-7 produces the most suitable results. Both used adsorbents are inexpensive, accessible, and treatable. This approach is economical and sustainable. Neem leaves, or Azadirachta indica, are discovered to be slightly more effective than bagasse made from treated sugar cane. The extent of water contamination can be controlled with the help of adsorption techniques.

As we can see from the entire study above, the primary findings are that the removal % drops as dye solution concentration rises. Additionally, the elimination percentage rises as agitation time increases. Here, it is also noted that the dose of adsorbent no longer significantly affects adsorption after a certain point.

Biodegradation process :-

In the current biodegradation studies, biodegradability could be determined based on a decrease in COD. The difference between the initial and final COD values can be regarded as being fairly representative of the actual biodegradable fraction and to be more representative of the actual biodegradability since any toxic or inhibiting effects would also become apparent from the analytical results. Using diluted samples from stock solutions and pre-growth acclimated heterogeneous bacterial cultures created from sludge, the biodegradation was conducted. Samples were analyzed at different intervals for COD to monitor the progress of biodegradation. COD reduction observed over a biodegradation period of 5-6 days for selected dyes. Two dyes were selected for biodegradation studies. [9]

Biodegradation of Malachite green dye solution

For this study pH is adjusted to 6.8-7.5, supplemented by nutrient and seeded with sludge. After a reaction period of about 5 days, the reactor contents were settled, the supernatant decanted and analyzed. COD removals were monitored daily during the course of biodegradation experiments.

Table. 4 **Biodegradation of Malachite Green dye**

Day	COD (mg/l)	Removal (%)
0	199	0
1	180	9.54
2	170	14.57
3	166	16.58
4	162	18.59
5	158	20.60
6	154	22.61

Results and discussions :-

In recent years, the industrial sector of the nation has experienced a rapid rise in water consumption. more so following the introduction of strategies for industrial development that have been liberalised. Rajasthan state-owned facilities are among the top textile printing facilities in the nation.

The results of the current investigation allow us to draw the conclusion that the biodegradation process can be utilised to remove colour from dyes used in the textile industry. The experiments were conducted in light of the COD shift. As may be seen, the results are rather inferior to the adsorption method. Therefore, it is recommended to combine the two techniques to increase the removal %.

Both methods are inexpensive, environmentally friendly, and don't produce any additional harmful consequences. the necessity for the future

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9. Treatment Of Dye Effluent (Specifically Congo Red Dye) From Textile Industries By Combination Of Biological And Physicochemical Methods Dr. Avnish Sharma Assistant Professor Department Of Chemistry Mlv Government College, Bhilwara (Raj) © 2016 JETIR August 2016, Volume 3, Issue 8 www.jetir.org (ISSN-2349-5162)