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Dye Wastewater Treatment by Green Chemistry: Various Methods

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Abstract

Textile mills use various dyes and discharge a large amount of colour rich waste water, which are not only hazardous for the human health but also effect environment adversely . These textile effluents are treated before discharge due to environmental issues. Waste water treatment in textile & dye industries involve the treatment of this colored wastewater in different concentrations. The major criterion used for this waste water treatment is coagulation. Wastewater mainly consisting of reactive dyes is treated with polyalluminium chloride, polyamine & poly DADMAC. The method is efficient for BOD and TSS but not effective for colour removal. This article presents the increasing practice and application of bio coagulants in spite of inorganic coagulants ferric, alum and organic coagulants like PAC, PloyDADMAC & polyamines. Bio coagulants mainly include seeds of *Azadirachta indica* (Neem), *Acanthocerus tetragonus* (Cactus), seeds of *Moringa Olifea* (Senjan) etc. use of bio-coagulants is very effective with almost 99 % colour removal for coagulant doses 300-1500mg/L. This dose is higher than chemical coagulants. Using focused beam of reflectance, sludge value of 50 ml/g was obtained for one and half hour. Bioformulation of chemical coagulants lowers the doses upto one third and also improved the performance upto 50%.

Keywords: Coagulation, Bio Coagulants, Focused Beam Reflectance, Sludge Value.

Introduction

Wastewater derived from the manufacture of dyes contains variety of compounds, raw materials e.g. aniline, intermediates and final product dyes itself similarly textile wastewater contains dyes in large amount and suspended solid also. In textile industries 20-300m^3 water is used per ton of textile produced thus these industries produce a large quantity of wastewater as a result of dyeing and other processes. Synthetic chemical dyes are also used in other industries like pulp and paper manufacture, paint , plastic and leather industries. Effluents of such industries are very toxic due to high TDS, presence of heavy metals, silica and nonbiodegradable dyes. Effluents of these industries are discharged into water bodies, thus is hazardous for aquatic organisms, human health and environment. It is necessary to decrease the quantity of dyes in the effluent before discharge or disposal and reusing the wastewater in an effective manner. Environment protection act, 1986 and other laws are endorsed for proper management of hazardous waste generated during the treatment of effluent. There are many approaches to treat this wastewater including Physical, chemical and biological etc. but they are costly and not eco-friendly.

Aim of the Study

Textile industries use various kinds of artificial dyes and discharge large amount of wastewater consisting many dyes.This waste water needs treatment before its disposal in water bodies due to environmental issues. Many biological and physicochemical methods are used for its treatment. The aim of study is to understand the methodology of processes and efficiency.

Dyes

Powder / Solid dyes may be basic such as Phodamine , malachite green. Victoria blue, bitsmarsk brown are salvent dyes. Liquid dyes are mainly Phodamine(l), crystal violet(l) and basic yellow(l) By products are NH3 , C6H5NH2 , N based organic compounds . Many of these dyes are toxic and are carcinogenic in nature. They impart imbalance on biological metabolism and thus destruct the aquatic and other ecosystem. Dye

waste water treatment is a difficult task as the dyes are recalcitrant organic molecules , resistant to aerobic digestion and stable to light /heat.

Characteristics of Effluents

The main parameters that characterize the dye waste water are

COD	:	Chemical oxygen demand
BOD	:	Biochemical oxygen demand
SS	:	Suspended solids
DS	:	Dissolved solids

Parameters which Clearly indicate the presence of dyes/other impurities and Odour

Total Solids

They include both suspended and dissolved solids. suspended solids are determined by filtering waste water sample . suspended solid include volatile suspended solids and fixed suspended solids.

pH

Acidic effluents may cause corrosion to the treatment scheme.

COD

Organic compounds are oxidized to H_2O and CO_2 by strong oxidizing agents.

BOD

It provides measurement of O_2 utilized by microorganisms which oxidise the organic compounds present in waste water . this test is direct measures of O_2 requirement and indirectly measure biodegradable organic matter.

Method to be applied for the treatment of wastewater depends on BOD and COD level of wastewater.

1. BOD/COD<2 indicates easily biodegradable nature .
2. BOD/COD>2 indicates not easily biodegradable nature.
3. Higher value of COD and presence of toxics and pollutants indicate not easily biodegradable and toxic nature.
4. Types of dyes / raw materials present.

Main motives of treatment methodology.

1. To provide an effective method for the treatment and disposal of waste water.
2. Including and enhancing recycle, reuse and recover.
3. It should be economic for small scale industries also.
4. It should be friendly for environment.

Chemical Method

Chemical methods consists of coagulation or flocculation combined with floatation, filtration, precipitation, electrokinetic coagulation, oxidation and electrochemical processes. These methods are expensive and not environment friendly. High electrical energy demand and consumption of chemical regents are also major problems.

Physical Method

These methods are highly effective in dye removal. Physical methods include sedimentation , screening, skimming and degastification. Adsorbents like activated carbon, coal, silica, clay, wood, cotton and other agriculture wastes are used for the treatment of waste water.

Biological Method

These methods are cheaper and simpler in application and environmentally friendly as they produce no secondary toxic sludge . Micro organism like Aspergillus niger, chlorella sp. , bacillus cereus mostly play important role in the dyes wastewater treatment. However such methods are limited in applications as they don't provide satisfactory colour removal, removal of toxic heavy metals , require large land area and nonbiodegradability of some dyes.

The aim of applying biological method in the treatment of wastewater is to reduce biological oxygen demand BOD. Under suitable environmental conditions, soluble organic substances of wastewater are oxidized completely. These methods include aerobic and anaerobic degradation depending upon the microorganisms involved in degradation. These processes are used separately and combinedly .

Primary treatment process

First step to treat wastewater is the removal of suspended solids, oil, grease etc.. Effluent is screened for coarse suspended materials like yarns, lint, fabric-pieces, rags using bar screens and fine screens.

Coagulation

It is an effective method to remove colour from dye wastewater coagulants are used as alum, clay, poly aluminum chloride (PAC), Aluminum chloride $AlCl_3$, $Al_2(SO_4)$, $FeCl_3$ and $FeSO_4$ etc. High doses are required and large amounts of sludge disposal creates secondary pollution problems. Polyamine and organic coagulants such as polydiallyl methyl ammonium chloride, poly DADMAC and poly amine have been proved to be effective alternatives to the inorganic coagulants and can enhance the removal of pollutants and toxicants from the waste water.

Flocculation

Flocculation is a gentle mixing stage which increase the particle size from sub microscopic micro floc to visible suspended particles. Microfloc particles collide causing them to bond to produce larger, visible flocs called pinflocs. By futher collisions and interaction with coagulants, macro flocs are formed.

Secondary treatment process

Removal of dyes and oil from the wastewater by the use of Microorganism in aerobic condition.

Tertiary Process

Final removal and purification process in which treated water is separated from sludge by passing through tertiary filter.

Advanced Oxidation Process (AOP)

Highly reactive and nonselective oxidizing agent OH^0 radical is generated by AOPs. OH^0 radical destroys the pollutants present in waste water, reacts in mild conditions and creates no secondary pollution various AOPs like O_3, UV, H_2O_2 provide efficient treatment of waste water. Ozone is artificially produced by UV-O_3 generators, vacuum – UV generators and cold plasma ozone generators. OH^0 free radicals are then produced due to the depletion of O_3 at pH>8 depletion of ozone increases with pH these radicals react with organic matter, micro organism, metal salts. O_3 reacts mainly by addition, substitution and ozonide formation. O_3 is strong

germicide and disinfectant. It is a strong oxidant which removes colour, odour, eliminates toxicants and assist in coagulation. 10% removal of COD is reported at pH8. Higher TOC and COD removal have been found on pH7. Odour removal of dye/textile waste water depends on initial COD. 95-99% colour removal has been found for COD 200-160 mg/L. Colour removal efficiency depends on temperature also. Peroxone, a mixture of H_2O_2 and O_3 is used for water waste treatment. H_2O_2 acting as a catalyst, accelerates the decomposition of O_3. At high pH H_2O_2 readily dissociates into HO_2. Which initiates the decomposition of O_3. It works efficiently at pH 7-10 colour removal rate is independent of PH but the COD removal does so H_2O_2 alone is not much effective in the treatment of dye wastewater at low or high pH. But under UV irradiation, H_2O_2 are Photolysed to produce OH^0 radicals which react with organic pollutants. It generates no sludge during the treatment, works under mild conditions & O_2 produced is utilized in aerobic decay processes. Colour removal by this process is efficient at low pH. Time taken in removal depends on the type of dye. For a 30 dyes 30-90 min has been reported. UV power if increased from 18 to 54 W, removal efficiency reaches to almost 100% Fenton's reagent (H_2O_2 / Fe^{2+}) produces OH^0 radicals in a large amount. Oxidation of organic compounds takes place in aqueous medium, colour removal efficiency increases with $FeSo_4$ amt TiO_2 /UV is preferred AOP due to its stability under various conditions. High radical production, efficiency, easy availability, low economy & high degradation efficiency.

Use of Biocoagulants

Moringa olifera contains various Phytochemicals which have medicinal uses. They are rich in glucosinolates and isothiocyanates. In ancient time, seed of moringa were used to treat suspicious water in northern Nigeria. Now newer biocoagulants, eg. seeds of Azadirachta indica (Neem) and pads of Acanthocereus tetragonus are used along with Moringa olifera and Cicer arietinum seeds. These biocoagulants were applied for the removal of congo red dye. Uses of these biocoagulants were found to be very effective and pH sensitive upto 99% dye removal was achieved for coagulant doses in the range of 300-1500 mg/L. though the doses of biocoagulants are higher than chemical coauants a satisfactory good value was obtained for sludge volume ~50ml/g for 1hr&30min respectively for both Acanthocereus and Moringa. Combining it with chemical coagulants lowered the doses and improved coagulatin efficiency upto 50%. The coagulation solution is prepared with moringa olifera seeds offered the removal of seed coats. Seeds are ground to powder, sieved and mixed with 0.5M NaCl solution. Temp. of wastewater initially 25.5^0c was 18.5^0c after the treatment. pH reaches from 9.5 to 7.2 & TDS from 309 ppm to 32 ppm offer the treatment. In a mixture of direct, acid and reactive dyes with individual concentration of 30ppm, colour removal is 82% with dose 25ml/L. This process is highly efficient for azo dyes as it removes upto 95% colour within 30-50 Min.

Use of Agricultural Waste

Various plants extracts of gum, guar, tannine, Moringa and cacti are used for dye removal. 73-87% colour removal efficiency has been reported at the pH 9.5. Strychni potatorum (Nirmali) seeds are efficient upto 80%. 98% colour removal efficiency has been reported about gum Arabic. Agriculture wastes are renewable, available in large amounts & cheap. They are better than chemical and other adsorbents as they need minimum or no processing. Prickly bark of cactus fruit is used as a low cost biomaterial for the dye waste water treatment. It is used specially to remove methylene blue from the aqueous solution by its adsorption on the PBCF. Raw material is dried in scen light for 15 days at room temp. ground to powder & sieved to obtain particles with size below 351 nm. PBCF surface area was studied by measuring Iodine number which was found to be 436. 25 ml of methylene blue dye was sparated by 0.1gm PBCF. By FTIR spectrum, equilibrium time for the sorption of MB into PBCF was found to be 60 Min. Sorption capacity was observed 222. 22 mg/g as according to Freundlich and Langmuir models. sorption increase with the dose of PBCF. Activated charcoal prepared by agricultural waste is the most popular material. It has low cos, high porosity, hence high sorption increases the removal efficiency. It is prepared by corn straw, wheat straw, rice straw , sawdust, cottons talk, coconut husk etc.

Conclusion

Many techniques are available to remove dyes from waste water such as coagulation, oxidation (chemical), filtration by membrane, microbial degradation, etc. These methods are efficient in colour removal but have many restrictions. Now a dyes adsorption is preferred over other methods due to being cheap and good colour removal efficiency oxidation is simple in application but H_2O_2 needs to be activated/ H_2O_2+Fe(II) generates sludge and hence secondary pollution. O_3 doesn't increase the amount of waste water but has short half life electro chemical destruction needs not any chemical but colour removal efficiency is not so high low cost adsorbents derived from agricultural wastes have been used for dye removal. Moringa seeds & AC obtained by agricultural wastes offer promising results with maximum efficiency and removal capacity.

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