Dye Waste Water Treatment, COD

Shloka Nayar[1]
[1]Nirma University, Ahmedabad, Gujarat

Abstract— The wastewater from textile industry and its treatment methods processes were tested and a general evaluation was made by compiling previous studies in literature.In different stages of textile industry, a significant quantity of water is consumed and this makes it necessary for regular control of textile wastewater. In order for textile wastewater not to deteriorate the environment and the lives of human beings, this water must be discharged after various treatment methods. It’s required to find the most suitable treatment method for textile wastewater which can minimize the production and investment costs of wastewater treatment plants.
Key words: Dye Waste Water Treatment, COD, BOD, Floatatioz

I. INTRODUCTION

The textile dyeing industry consumes huge quantities of water and produces large volumes of wastewater from various steps in the dyeing processes. Waste water from printing and dyeing units is usually rich in colour containing residues of reactive dyes and chemicals. These components are aerosols, high chroma, high COD and BOD concentration as well as much more hard-degradation materials. The toxic effects of dyes and other organic compounds, along with acidic and alkaline contaminants, from industries on the general public are widely accepted.The dyes are mainly aromatic or heterocyclic compounds, with colour-containing groups and polar groups. The structure is complicated and stable, resulting in higher difficulty to degrade the wastewater. The environmental impacts of the textile industry have been recognized for some time, both in terms of the discharge of pollutants and of the consumption of huge amount water and energy. Environmental problems of the textile industry are primarily caused by the discharge of wastewater. The textile sector has a high water demand and Its biggest impact on the environment is related to waste water .Therefore, reuse of the effluents represents an economical and ecological challenge for the textile sector. Textile processing employs a number of chemicals, depending on the type of the raw material and product The effluents resulting from these processes vary greatly in composition due to differences in processes, fabrics and machinery. [1]

II. WASTE WATER TREATMENT PROCESSES

The dye wastewater has a huge amount of complex components having high concentrations of organic, high-colour.Due to their high COD, their coloration and their salt content, the wastewater resulting from dyeing cotton using reactive dyes are dangerously polluted.As aquatic organisms need light to develop, any lacking in this respect caused by colored water can lead to an imbalance of the ecosystem.Also, the water of rivers that is used as drinking water must not be colored, as the treatment costs will be increased.Studies related to the feasibility of treating dyeing wastewater are very important.

In the past several decades, a number of techniques have been developed for finding an economic and efficient way to treat the dye wastewater.These techniques include physicochemical, biochemical, combined treatment processes and other technologies. These technologies are highly efficient for the treatment of textile dyeing wastewater.[2]

A. *Conventional methods:*

Wastewater treatment is an amalgamation of unit processes, some physical and others chemical or biological in their action. A conventional treatment process consists of a series of individual unit processes, in which the output (or effluent) of one process becomes the input (influent) of the next process. The first stage is usually made up of a physical process.

Physicochemical wastewater treatment is widely used in the sewage treatment plant.It has a high removal of chroma and suspended substances and low removal of COD. The common physicochemical methods are as follows. [3]

1) *Equalization and homogenization:*

Because of water quality being highly polluted and quantity fluctuations, presence of complex components, textile dyeing wastewater generally requires pretreatment to ensure effective treatment and stable operation. In general, a regulating tank is set to treat the wastewater. Meantime, to prevent the lint, cotton seed shell, and the slurry from Settling to the bottom of the tank, it’s usually mixed the wastewater with air. The hydraulic retention time is generally about 8 h. [4]

2) *Floatation:*

The floatation process produces a huge number of micro-bubbles to form the three-phase substances of gas,water and solid. Dissolved air under pressure is added to cause the formation of tiny bubbles which get attached to the particles. Under the effect of interfacial tension, buoyancy of the rising bubble, hydrostatic pressure and number of other forces, the microbubble will adhere to the fibers. Due to its low density, the mixtures float onto the surface so and thus, oil particles are separated from the water.This method can effectively remove fibers in wastewater.[5]

3) *Coagulation flocculation and sedimentation:*

Coagulation flocculation sedimentation is one of the most common methods, especially in the conventional waste water treatment process.It’s active on suspended matter and colloidal particles. Their electrical charge gives repulsion and prevent aggregation. Addition of water in electrolytic products such as aluminum sulphate, ferric sulphate giving hydrolysable metallic ions can eliminate the surface electrical charges of the colloids. This method is named coagulation. Normally the colloids contain negative charges, so the coagulants used are usually inorganic or organic cationic coagulants (with positive charge in water). The metallic hydroxides and the organic polymers,apart from giving the coagulation,also help the particle to aggregate into flocks, thereby increasing the sedimentation rate. The combined action of coagulation, flocculation and sedimentation is named clariflocculation. Settling needs stillness and flocculation needs flow velocity, so these three processes need different reactions tanks. This process uses mechanical separation among heterogeneous matter, while the dissolved matter is not well removed (clariflocculation eliminates a part of it by absorption into flocks). The dissolved matter can be removed better by biological or by other physical chemical processes. But higher chemical load on the effluent (which normally increases salt concentration) increases the sludge formation and leads to uncomplete dye removal. [6]

4) Biological method:

Biological treatment is the most economical alternatives as compared to the other physical and chemical processes. Biodegradation methods like fungal decolourization, microbial degradation, adsorption by microbial biomass and bioremediation systems are often used for the treatment of industrial effluents because many microorganisms such as bacteria, yeasts, algae's and fungi are capable of accumulating and degrading different pollutants.

Biological methods help in removing pollutants from waste water by using natural processes involving bacteria and other micro organism for the oxidation of organic waste. Biological methods are generally cheap,easy to apply and are currently used to remove organic matter and colour from dyeing and textile waste water. Most of the existing processes include an initial step of activated sludge treatment to remove the organic matter which is followed by oxidation. But these methods are less preferred due to the low biodegradability of dyes.[7]

B. Advanced methods:

1) Adsorption:

Adsorption is the most common method in physicochemical wastewater treatment, which involves the mixing of wastewater and a porous material powder or granules, such as activated carbon and clay, or let the wastewater pass through its filter bed composed of granular materials.In this method,the pollutants in wastewater are adsorbed and removed on the surface of a porous material or filter.The commonly used adsorbents are activated carbon, silicon polymers and kaolin.Adsorbents have selective adsorption of dyes. But, so far, activated carbon is the best adsorbent known for dye wastewater. It can remove chroma upto 92.17% and COD can be reduced 91.15% in series adsorption reactors. Because activated carbon has good selectivity.It effectively removes the water-soluble dyes in wastewater, such as reactive dyes, basic dyes and azo dyes, but it cannot adsorb the suspended solids and insoluble dyes. Moreover, activated carbon can not be directly used in original textile dyeing wastewater treatment, while generally it's used in lower concentration of dye wastewater treatment or advanced treatment because of the high cost of regeneration. Dissolved organics are adsorbed on the surface as waste water containing them is made to pass through the adsorbent. Most commonly used adsorbent for treatment is activated carbon. It is manufactured from carbonaceous material like wood, coal, petroleum products etc. A char is made by burning a material in the absence of air. The char is then oxidized at a higher temperature to create a porous solid mass which has large surface area per unit mass. The pores need to be large enough for soluble organic compounds to diffuse in order to reach the abundant surface area. Typical properties of commercially available activated carbon are given in Table 1. [8]

PARAMETER	VALUE
Base material	Lignin
Real density	1.9 g/cm^3
Apparent density	.244 g/cm^3
Surface area	750 m^2/g
Iodine value	93
Effective pore size	2 micron

Table 1: Properties of typical activated carbon[8]

The activated carbon once it is saturated needs replacement or regeneration. Regeneration is done chemically or thermally. The chemical regeneration can be done in within the column itself either with acid or other oxidizing chemicals. This normally effects partial recovery of activity and makes frequent recharging of carbon necessary. For thermal regeneration, the exhausted adsorbent is transported preferably in water slurry to a regeneration unit where it is dewatered and fed to furnace and heated in controlled conditions. This process volatilizes and oxidizes the impurities held in carbon. The hot reactivated carbon is quenched with water and moved back to the site. This results in almost complete restoration of its adsorption. There are some other materials such as activated clay, silica, flyash, etc are also known to be promising adsorbents.[9]

2) Ion Exchange:

Ion exchange process is used for the removal of inorganic salts and some specific organic anionic compounds such as phenol. All salts are made of a positive ion of a base and a negative ion of an acid. Ion exchange materials are capable of exchanging soluble ions and cations with electrolyte solutions. For example, when a cation exchanger in the sodium form is contacted with a solution of calcium chloride, it scavenges the calcium ions from the solution and replaces them with sodium ions. This provides a convenient way for removing the hardness from water or effluent. Ion exchange resins are available in several such as natural zeolit, synthetics which may be phenolic , sulphonic styrenes and other complex compounds. The divalent ions like calcium and magnesium in general have high affinity for ion exchange resins and can be removed with high efficiencies.

In the ion exchange process, impurities from the effluent streams is transformed into another one of relatively more concentration with increased quantity of impurities because of the addition of regeneration chemicals. This process is not used for removal of non-ionic compounds. [10]

3) Chemical Oxidation:

Chemical processes, as the name suggests, are those in which chemical reactions occur, for eg. precipitation. Chemical treatment relies mainly upon the chemical interactions of the contaminants that we wish to remove from water, and the application of chemicals that either aid the separation of contaminants from water, or help in the destruction or neutralization of toxic effects associated with contaminants. Chemical treatment methods can applied both as stand-alone technologies or as an integral part of the treatment process with physical,chemical operations can oxidize the pigment in the printing and dyeing wastewater as well as bleaching the effluent. Currently, Fenton oxidation and ozone oxidation are commonly used in the wastewater treatment. [11]

4) Fenton reaction :

Oxidative processes are a widely used chemical method for treating textile effluent, especially where decolourisation is the main concern.The main oxidizing agent is hydrogen peroxide (H_2O_2), variously activated to form hydroxyl radicals.These are among the strongest existing oxidizing agents and are capable of decolourizing a wide range of dyes.

The first method to activate hydroxyl radical formation from H_2O_2 is called the Fenton reaction, where hydrogen peroxide is added to an acidic solution (pH=2-3) containing Fe^{2+} ions. Fenton reaction is used as a pre-treatment for wastewater resistant to biological treatment or/and toxic to biomass. The reaction is exothermic in nature and should be carried out at a temperature higher than ambient.However, in large scale plants, the reaction is commonly carried out at ambient temperature using large excess of iron as well as hydrogen peroxide. In these conditions ions do not act as catalysts and a great amount of total COD removed has to be ascribed to the $Fe(OH)_3$ co-precipitation. The main drawbacks of this method are the significant addition of acid and alkali to reach the required pH, the necessity to abate the residual iron concentration, too high for discharge in final effluent, and the related high sludge production.[12]

5) Ozone oxidation :

Chemical reagents and biological methods have been in use for a long time for the treatment of wastewater, even though it has resulted in further pollution. A much more efficient way to handle dye wastewater is to use ozone. Due to its strong oxidation properties, ozone has proved to be appropriate when treating wastewater. The use of ozone in wastewater treatment is an environmentally friendly way to deal with wastewater.It is a very effective and fast decolourising treatment, which easily breaks the double bonds present in the dyes. Ozonation can also destroy the foaming properties of the residual surfactants and it can oxidize a good portion of COD. It can also improve the biodegradability of effluents which contains a high fraction of non biodegradable and toxic components through the conversion (by a limited oxidation) of recalcitrant pollutants into more easily biodegradable intermediates. As a further advantage,the treatment increases neither the volume of wastewater nor the sludge mass. Full scale applications are growing in number, mainly as final polishing treatment, generally requiring up-stream treatments such as at least filtration to reduce the suspended solids contents and improve the efficiency of decolourisation. Sodium hypochlorite has been widely used in the past as oxidizing agent. In textile effluent it initiates and accelerates azo bond cleavage. The negative effect is the release of carcinogenic aromatic amines and otherwise toxic molecules and, therefore, it should not be used.

Also known as AOP , these processes use ozone in combination with peroxide , UV or reactions under high pH .Hydrogen peroxide is an oxidant whereas UV is not.But when used with Ozone, the breakdown of organics to CO_2 and H_2O is facilitated. The reaction pathways are many but for easy understanding the main and the most common pathway would be when Hydrogen Peroxide decomposes into Hydroxyl radicals in the presence of ozone or UV. There exists in solution a combination of ozone molecules in high oxidative state and free radicals also in very high oxidative state. The combination is highly reactive as the free radicals which are capable of withdrawing atoms (often hydrogen) from a substrate. The role of hydrogen peroxide in AOP is to make the pollutant more available to ozone attack and also aids the overall oxidation UV lights provides energy to break chemical bonds .This makes the other fragments more susceptible to ozone attack .UV light also converts H_2O_2 to a highly reactive hydroxyl radical and the generation of oxygen . UV lamps are thus used as ozone distructing agents as it helps convert ozone into molecular oxygen.

An easy way to explain ozone oxidation would be to break the process into:

(1) Preliminary treatment consisting of processes such as screening
(2) Primary treatment which includes sedimentation
(3) Secondary treatment ehich includes activated sludge treatment and secondary sedimentation.
(4) Tertiary treatment which includes discoloration, disinfection ,COD reduction etc

Ozone in the preliminary stage is used for detoxification .At the secondary stage it's is used for sludge reduction and during the tertiary stage is used for disinfection, micro pollutant removal, COD reduction and decoloration.

In each of these situations the use of ozone has been found to be very productive .

(1) Decolourisation & Deodorization
(2) De toxification
(3) Disinfection
(4) COD/BOD reduction
(5) Sludge Reduction

6) Basic Principal:

ozonation changes solid waste problems to treatable liquid waste .The cell wall of bacteria attacked by ozone and lysis of cell wall occurs .The Cellular contents are liberated (COD) .This liberated COD is then returned to the basin where the bacteria feed on this COD. Consequently sludge reduction occurs.The reduction of sludge can be as high as 40% to 45% with an ozone dose of 0.01 to 0.1gram of ozone per Kg of solids removed.

The additional properties achieved by ozonation would be elimination of foaming problems ,a positive impact on color and surfactants and a dramatic reduction in filamentous bacteria

Therefore,it can be concluded that ozone technology in waste water treatment :

- Is a residual free treatment technology

- It is used for various applications (field proven for decades but also new emerging
  - applications)
- OZONE is a specific tool but not a stand alone concept,
- OZONE is very effective if applied properly and in combination with especially biological treatment .[13]

7) Membrane separation processes:

Membrane separation process is a method that uses the membrane's micropores in order to filter and uses membrane's selective permeability for separation of certain substances in wastewater.The membrane separation process is often used for treatment of dyeing wastewater mainly based on membrane pressure, such as reverse osmosis, ultrafiltration, nanofiltration and microfiltration. Membrane separation process is a new separation technology, with high separation efficiency, low energy consumption, easy operation, no pollution and so on. However, this technology is still not large-scale promoted because it has the limitation of requiring special equipment, and having high investment and the membrane fouling and so on.[14]

8) Reverse osmosis

The process of reverse osmosis is based on the ability of certain specific polymeric membranes, usually cellulose acetate or nylon to pass pure water at fairly high rates and to reject salts. To achieve this, water or waste water stream is passed at high pressures through the membrane. The applied pressures has to be high enough to overcome the osmotic pressure of the stream, and to provide a pressure driving force for water to flow from the reject compartment through the membrane into the clear water compartment.In a typical reverse osmosis system, the feed water is pumped through a pretreatment section which removes suspended solids and if necessary, ions such as iron and magnesium which may foul the system. The feed water is then pressurised and sent through the reverse osmosis modules. Clear water permeates through the membrane under the pressure driving force, emerging at atmospheric pressure. The pressure of reject stream is reduced by a power recovery, which helps drive the high pressure pump and then is discharged.Reverse osmosis can be used as end-of-pipe treatment and recycling system for effluent. After primary, secondary and/or tertiary treatment, further purification by removal of organics and dissolved salts is possible by use of reverse osmosis. Scale causing constituents such as hardness,carbonate,silica,heavy metals, oil etc has to be removed from the feed. As the membranes are sensitive to oxidizing agents like chlorine or ozone, they should also be absent.Reverse osmosis membranes are available in different configurations. In spiral wound system, membrane and supporting material are placed in alternate layers, rolled into a cylindrical shape and inhoused in tube of suitable martial. The support material is porous and serves as transport medium for permeate. Tubular systems are available in which the membrane and its support are wound to fit inside a containment tube. Permeate is withdrawn from the support medium, while reject passes through the core of the membrane. Hollow fiber membranes are extremely small tubes. These fibres can be suspended in the fluid without the use of support medium. The feed water is usually on out side of fibre, while the permeate is withdrawn through the centre. The disc module is relatively new in the reverse osmosis application. Unlike conventional membrane modules such as spiral wound, the design of disc module facilitates an open feed flow path over membrane element. The membrane is housed in hydraulic disc which works as membrane spacers. [14]

9) Nanofiltration:

Nanofiltration has been applied for the treatment of colored effluents from the textile industry. Its aperture is only about several nanometers, the retention molecular weight by which is about 80-1000da, A combination of adsorption and nanofiltration can be adopted for the treatment of textile dye effluents. The adsorption step precedes nanofiltration, because this sequence decreases concentration polarization during the filtration process, which increases the process output. Nanofiltration membranes retain low molecular weight organic compounds, divalent ions, large monovalent ions, hydrolyzedreactive dyes, and dyeing auxiliaries. Harmful effects of high concentrations of dye and salts in dye house effluents have frequently been reported. In most published studies concerning dye house effluents, the concentration of mineral salts does not exceed 20 g/L, and the concentration of dyestuff does not exceed 1.5 g/L. Generally, the effluents are reconstituted with only one dye, and the volume studied is also low.The treatment of dyeing wastewater by nanofiltration represents one of the rare applications possible for the treatment of solutions with highly concentrated and complex solutions.A major problem is the accumulation of dissolved solids, which makes discharging the treated effluents into water streams impossible. Various research groups have tried to develop economically feasible technologies for effective treatment of dye effluents. Nanofiltration treatment as an alternative has been found to be fairly satisfactory. The technique is also favorable in terms of environmental regulating. [15]

10) Ultrafiltration:

Ultrafiltration whose aperture is only about 1nm-0.05μm, enables elimination of macromolecules and particles, but the elimination of polluting substances, such as dyes, is never complete. Even in the best of cases, the quality of the treated wastewater does not permit its reuse for sensitive processes, such as dyeing of textile. 40% of the water treated by ultrafiltration can be recycled to feed processes termed "minor" in the textile industry (rinsing, washing) in which salinity is not a problem. Ultrafiltration can only be used as a pretreatment for reverse osmosis or in combination with a biological reactor.[16]

11) Microfiltration:

Microfiltration whose aperture is about 0.1-1μm is suitable for treating dye baths containing pigment dyes, as well as for subsequent rinsing baths. The chemicals used in dye bath, which are not filtered by microfiltration, will remain in the bath. Microfiltration can also be used as a pretreatment for nanofiltration or reverse osmosis.[17]

Process	**Pore size(micron)**	**Molecular weight**	**Used for removal of**
Microfiltration	.007-2.00	>100000	Bacteria,pigments ,oil etc

Ultrafiltration	.002-.10	1000-200000	Colliods
Nanofiltration	.001-.007	180-15000	Dyes,diavalent ions
Reverse osmosis	<.001	<200	Salts and ions

Table 3: Filtration spectrum of different membranes

III. SELECTION OF ADVANCED TREATMENT METHODS

Proper selection and application of individual or combination the advance treatment methods in textile industry can effectively make recovery of water and/or salts from effluent streams for their reuse in production process. Along with the recovery and reuse of water and salt, the advance methods can also be applied to meet stringent environmental or regulatory requirements such as zero effluent discharge .

- According to the colour removing datas it has been stated that Fenton process is more suitable for removing colour from textile wastewater than any other oxidation process.
- Colour removal is not provided by biological methods.
- Membrane process is a new technology which is widely used in refining of wastewater. These methods are usually used following Adsorption or oxidation methods. Membrane filtrations can produce treated water with high purity. Treatment system like activated carbon adsorption and ozonation can be used to make the effluent suitable for use in membrane filtration.
- Evaporation system can be used for minimizing effluent volume or achieving desired concentration of target pollutant. The evaporation system and crystallizer combination can recover salt.[18]

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