Removal Methods of Synthetic Dyes from Industrial Wastewater: A review

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Abstract

The textile industry has significant impacts on water through discharging effluents into various receiving bodies involving rivers, ponds and other public sewer. The main contaminants produced by textile industries are from several of their wet-processing such as scouring, bleaching, mercerizing and dyeing. Dyeing process normally uses large amount of water for dyeing, fixing and washing processes. Dyes are using in several industries, like paper-making, textiles, plastic and foods industries. Wastewater contains dye has become one of the most pollution sources. The textile effluent treatment involves mainly physical, chemical and biological methods. Several treatment technologies are using now a days for removal of dye from industrial wastewater including coagulation, adsorption, biological methods, advanced oxidation processes (AOPs), membrane technology and electrochemical methods. Removal of dyes from industrial wastewater using various methods has been reviewed in this paper.

Keywords: wastewater, dyes, adsorption, coagulation, advanced oxidation processes (AOPs), biological methods, membrane technology, electrochemical methods.
Introduction

One of the most important sources of pollution in water, soil and environment is Industrial wastewater. It is effects on the ecosystem in addition to its effects on human life. So it is very important to treat the industrial wastewater before discharge into the ecosystem [1]. The great part of pollution in textile wastewater come from dyes and finishing processes [2]. In textile wastewater, dye is a component that imparts color and is difficult to treat by traditional processes [3]. At present, the public has become more sensitive to environmental protection and public awareness has increased about the potential harmful effects of industrial waste residues contaminated with various pollutants, including dyes on the environment [4]. Dyes can be defined as substances that, when applied to a substrate, provide color through a process which change at least tentatively any crystalline structure of colors substances. It is widely used in many industries such as the textile, food, cosmetic, pharmaceutical, photography, plastics and paper. The dyes are classified according to their chemical and structure application, and consist of a group of atoms known as chromospheres, responsible for color of dye. Gradually, dyes appear as a class of anthropogenic organic substances that pose a serious threat to the environment [5, 6]. The wastewater which containing dyes is usually discharged directly into nearby rivers, drains, stagnant, ponds or lakes. Dyes will Absorbs and reflect sunlight entering the water and thus can interfere with the growth of bacteria and impede photosynthesis in aquatic plants [7]. Most dyes most dyes have complex aromatic structure which resistance of biological activity, light, ozone and other degradation environment and are therefore not easily removed by traditional waste treatment processes [8]. The production of wastewater contains dye has increased rapidly in recent years. It is investigated that more than 100,000 tons of dyes are produced in each year and about 10% of the dyes are discharged into the ecosystem, causing significant damage to human health and aquatic organisms. In the process of producing of dyes many substances are used as raw materials such as benzene, naphthalene, anthraquinone in addition to other compounds and its usually chelate with minerals or salts to generate wastewater containing salts, acids, alkali, halogen, hydrocarbons, nitro, amines, dyes and other substances [9]. The chemical categories of dyes used more frequently on an industrial scale are the azo, anthraquinone, sulfur, indigoid, triphenylmethyl (trityl), and phthalocyanine derivatives. However, it must be emphasized that the vast majority of synthetic dyes currently used in this industry are AZO derivatives [10]. Several physical and chemical methods are employed for treating of textile industry effluents, included ozonation, coagulation, flocculation and biological treatment. The physical and chemical processes disadvantages are the formation of sludge and the disposal of sludge and the necessary space. The disadvantages of biological processes are the presence of heavy toxic metals that hinder the growth of microorganisms, and most dye used are nondegradable in nature and need more for treatment [11,12]. The present paper deals with the types of dyes and methods of removal.

Type of dyes

Dye wastes is one of the most problematic contaminants because it can be readily identified by the human eye and cannot be easily decomposed [13]

The dyes used in the Textile industry are classified as

Below:-
1. Cationic dyes- include basic dyes.
2. Anionic dyes- include acid dyes, reactive dyes, azo dyes, direct dyes.
3. Non-ionic dyes- includes disperse dyes that do not ionize in aqueous media[14, 15].

Azo dye is considerable as the biggest group of dyes, with -N=N- as a chromophore in an aromatic system. There are disazo, trisazo, monazo, polyazo and tetrakisazo dyes relying on the number of existing of Azo groups. Anthraquinone is the fundamental unit of this class of dyes. It is faint yellow in color which could be used a dye but it cannot be classified as a dye. Dyes which contain anthraquinone unit belong to disperse, mordant and vat dyes. Generally disperse dyes use to dye nylon, cellulose acetate and other hydrophobic fibers [16].

Removal Methods of dyes

1-Adsorption

Adsorption is an essential process in the physiochemical treatment of wastewater, a treatment that can economically meet current effluent standards and water reuse requirements. Adsorption is a mass transfer process involving the accumulation of substances in a two phases interface, such as a liquid interface, liquid- gas, gas - solid, or solid - liquid. The substance being adsorbed is called adsorbate and the adsorbing material is described the adsorbent. The driving force of adsorption is surface affinity, pH, surface area and Chemical reactivity for adsorption per volume unit and reduction of surface tension are the main parameter of adsorption [18, 17]. Adsorption is a process in which the molecules of any state (gas or liquid) concentrate on the surface conduction without any interaction and it’s considered as the most effluent methods for removing of dyes from industrial wastewater by treatment due to ease of operation, low cost and efficiency [19]. It has been pointed that the adsorption is an effective and attractive method because it can completely remove various types of dyes without leaving any fragments in the effluent [20]. Adsorption depending on the nature of the adsorbate such as molecular structure, molecular weight, molecular size, polarity and solution concentration. In addition it also depends on the surface properties of the adsorbent material such as particle size, surface area, surface charge, etc. The process of adsorption is a highly efficient separation technique and is superior to other technologies available for wastewater treatment in terms of initial cost, simplicity of design, ease of operation and non-toxic materials. The efficiency of the adsorption process depends on the physical and chemical properties of the adsorbents and adsorbate. Adsorbent’s selectivity depends on adsorption capacity, surface area, availability, and total cost [21]. Commercial activated carbon is the most widely used as a adsorbent material in the dyes removal [21, 22 and 23]. The selection of adsorbents depends on several factors (concentration and type of microstructure, efficiency / cost ratio, adsorption capacity, and high selectivity of a large amount of water). Moreover, these adsorbents should be non-toxic, low-cost, renewable, easily recoverable from alters, readily available, It should lead to zero waste sludge [24]. An adsorbent material is a substance, usually porous in nature with a high surface area that can adsorb material on its surface by the intermolecular forces. Adsorbents are usually used in the form of spherical pellets, rods, moldings, or monoliths with hydrodynamic diameters between 0.5 and 10 mm.
They must have high resistance to abrasion, high thermal stability and small pore diameters, resulting in higher open surface area and therefore higher surface adsorption capacity. Adsorbents should also contain a distinct pore structure that allows the rapid transfer of gaseous vapors [25]. The adsorbents are mainly derived from sources such as zeolite, coal, clay, ores and other waste resources. The adsorbents prepared from the waste resources used include petroleum wastes, coconut shell tannin-rich materials, sawdust, fertilizer waste, sugar industry wastes, blast furnace slag, chitosan and seafood residues, seaweed, algae, scrap tyres, fruit wastes and peat moss as well as other adsorbents such as commercial activated carbon (CAC) [26, 27]. In addition to the mentioned above many natural materials were used as natural adsorbents such as orange peel as adsorbent for the removal of dyes from wastewater and to establish it as a standard wastewater treatment process for composite knit industry[28], rice husk[29], activated carbon[30], fly ash[31], papaya leaf[32], natural zeolite[33], chitosan films[34], calotropispingantia [35], novel nonconventional activated carbon[36], peanut shell powder[37], cow dung ash[38], agricultural waste[39], sugar can stalks[40], modified pumice stone[41],quartenised sugar cane bagasse[42], nano aluminum oxyhydroxide[43] and ferric oxide[44].

1-1-Factor affecting adsorption

Adsorption of dye can be affected by many factors such as contact time, pH dosage of adsorbent and initial dye concentration. Dye removal rate increase as contact time increase in to a certain extent [46, 45]. in general, the increase in dye removal along with the increasing of adsorbent dose, where the amount of sorption site at the adsorbent surface will increase by increase of adsorbent dosage that will result on the increase of dye removal percentage . The pH is very significant factor for adsorption of dye in the process of adsorption [46].

1-2-Adsorption Isotherms

1-2-1-Langmuir isotherm

Langmuir isotherm can be obtain by following equations [47].

\[ q_e = Q_o b C_e (1 + b C_e) \]  \( \text{equation 1} \)

\[ \frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{b Q_o C_e} \]  \( \text{equation 2} \)

Where:
- \( q_e \) is the adsorbed amount of dye per unit weight of adsorbents
- \( C_e \) is the concentration of the adsorbate at equilibrium (mg/L).
- Langmuir constants, \( Q_o \) and \( b \) are related to maximum adsorption capacity and energy of adsorption through
the Arrhenius equation, respectively.
When m/x or 1/qe is plotted against 1/Ce, a straight line with slope
1/b Qo is obtained and intercept is correspond to
1/Qo. The Basic characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor, r,
which describes the type of isotherm and is defined as following equation:

\[ r = \frac{1}{1 + b C_0} \]  

**1-2-2-Freundlich isotherm**

Freundlich isotherm can be obtain by following equations [47].

\[ Q = K_f C_e^{1/n} \]  
\[ \log q_e = \log K_f + \frac{1}{n} \log C_e \]

Where
K_f and n are the Freundlich constants
that are associated with adsorption capacity and
adsorption intensity, respectively. The value of n
between 2 and 10 shows good adsorption. The
other parameters have been defined as in equation
(1) and (2)

**2- Advanced oxidation processes (AOPs)**

Synthetic dye wastes discharged from several industrial processes pose a major threat to the environment due to the risk of
toxicity to aquatic organisms in natural water resources and inhibition of photosynthetic activity. Many researchers
proposed advanced oxidation processes (Ozone, H2O2, TiO2, ZnO, RuO2, SiO2 and UV) as a reasonable option for
efficient removal of color pollutants from wastewater. Advanced oxidation processes including TiO2 / UV and H2O / UV
were demonstrate for their potential use in dye removal from textile wastewater [48, 49]. Advanced Oxidation Process
(AOP) is a chemical treatment method that grows in the wastewater management industry. It is suggested way to remove
organic matter. The basic principle of AOP includes the production of hydroxyl radicals (OH •), which can be generated
from hydrogen peroxide (H2O2), ozone, photo-catalysis or oxidizing agents together with the use of ultraviolet rays. The
OH • is primarily responsible for the decomposition of organic compounds [50]. Advanced oxidation processes (AOPs)
have already been used to treat wastewater containing t organic matters such as, surfactants, insecticides, coloring matters,
pharmaceuticals and endocrine disrupting chemicals. In addition, they have been successfully used as pre-treatment
methods to reduce concentrations of toxic organic compounds that inhibit biological wastewater treatment [51, 52]. The most common advanced oxidation processes (AOPs) of treatment is using of UV wavelengths (200-300) nm at 254 nm to disassociate H2O2 progressively. The UV/H2O2 systems generate hydroxyl radicals (OH•), which are highly powerful oxidizing species [53]. The main advantages of advanced oxidation processes involve the lack of by-products that may cause secondary pollution, elimination of the hazard of overdosing the oxidizing agents, and high process rate and efficiency [54].

2-1-Ozone (O3)

Ozone is one of the most powerful and commercially available oxidizing substances and is commonly used for municipal water treatment and wastewater. In addition to the oxidizing capabilities of ozone, it is considered as an environmentally friendly method of treatment. Contaminants, colored substances, odors and microorganisms are destroyed directly by oxidation, without creating harmful chlorinated by-products or significant residues [55]. Ozonation is particularly attractive for wastewater treatment because ozone is soluble in water and can decompose quickly to form several free radicals including OH• (hydroxyl), HO3•, HO4• and O2− (superoxide). Such free radicals are readily available to react instantly with any organic compounds present in water, like the dyes [56]. Therefore, the using combination of ozonation and biological degradation process may provide more economical and effective process in the treatment of highly colored wastewater [57].

2-2-Fenton Oxidation Technology

Among several of AOPs, the Fenton reagent (H2O2 / Fe2 +) is one of the most effective ways to oxidize of organic pollutants. The Fenton reagent has been found to be effective for treating of various industrial wastewater compounds, including aromatic amines, a wide range of dyes, and different other substances, e.g. pesticides and surfactants insecticides. Therefore, the Fenton reagent has been applied for treating a variety of waste such as those associated with textile and chemical industries [58]. Fenton process is based on OH production as a result of interaction between Fe2 + and H2O2 under acidic conditions. The process was improved using different sources of iron such as iron powder. The reaction of Fenton, in which Fe0 is used mainly, can be implemented in two ways, the one is oxidation of the pollutant as a result of H2O2 reaction on the iron surface, and the other one is oxidation of the contaminated H2O2 reaction with Fe2 +, which is transferred to the liquid phase by dissolving on the iron surface [59]. The Fenton reagent was found to target water-soluble, nucleophilic and aromatic contaminants [60].

2-3-Ultraviolet Lamp

Ultraviolet light is a part of the spectrum light. The process usually includes using of low-pressure UV lamps with a principal wavelength of 254 nm. The maximum absorption of ozone molecules is at 253.7 nm, the light source commonly used is a medium-pressure mercury lamp wrapped in a quartz sleeve that can generate the UV light at wavelength of 200-280 nm. Application of UV lamp for textile wastewater treatment with two different UV radiations; 150W, \(\lambda=254-578\) nm and 15W, \(\lambda=254\) nm, to the synthetic textile wastewater for 1 to 3 showed significant reduction (47 to 30%) in microbial inhibitory action for optimum radiation time of 1 hour [61].
2-4-Peroxone (H2O2/O3)

H2O2 acts as a catalyst and accelerates the decomposition of ozone to hydroxyl radical when a mixture of hydrogen peroxide and ozone is used to treat wastewater. At acidic pH, H2O2 reacts very slowly with O3 whereas at high pH the dissociation of H2O2 into HO2 [62].

3-Coagulation

Coagulation and flocculation is widely used as physicochemical methods for treating of industrial wastewater because it removes colloidal particles, very fine solid suspensions and some soluble compounds initially existing in the wastewater by destabilization and formation of flocs. These methods are effective and easy to operate [63, 64]. Coagulation is mostly applied in textile industries. Because this method is effective to remove a large amount of COD and color [65]. Coagulation is one of the most common unit operations in water and wastewater treatment trains. It is also one of the most efficient treatment methods for removing dyes from industrial wastewater [66]. Various researchers pointed that the coagulation process proved to be the most effective method in comparison to other processes like anaerobic reduction, oxidation and adsorption [67]. Coagulation can significantly reduce the concentration of contaminants in wastewater. About 70 to 80% removal of color and similar reduction in the concentration of organic compounds can be achieved. This is one of the simplest and cheapest methods that can be easily applied in industrial installations [68]. Wastewater discharging from dye industry is can be treated by combination process of biological treatment and coagulation treatment. Coagulation can reduce the wastewater loading and thus reduce the treatment cost [69]. The efficiency of this method depending on the properties of raw wastewater, temperature and pH of the solution in addition to the type and dosage of coagulants, and duration of mixing [70, 71 and 72]. Typical coagulant are inorganic salt such as Al (SO4)3 or FeCl3, ferric chloride, as well as synthetic organic polymer. Although these chemicals are effective for removing of dyes and suspended matters from the aqueous solution, many disadvantages have been pointed recently, such as their impact on human through causing diseases such as Alzheimer’s which is caused by inorganic salts. Also, the synthetic organic polymers such as acrylic amide or polyacrylamides have neurotoxin and carcinogenic effects [73, 74, 75 and 76]. The major advantage of the coagulation and flocculation processes is decolourization of textile wastewater that can be accomplished through dye molecules removal from the effluents, and not by partial decomposition of dyes, which could produce potentially harmful and toxic aromatic compounds [77].

4-Biological methods

In last year’s there has been widespread interest and numerous studies on the use of biological methods using microorganisms such as fungi, bacteria and algae which are highly capable to biodegrade and biosorb of dyes in wastewater. Application of microorganisms for removing of dyes from wastewater offers significant advantages such as relatively low-cost, environmentally friendly process, produces less secondary sludge and final products for complete mineralization are not toxic. Many research has been done and demonstrate the potential of microorganisms such as Cunninghamellaelegans, Aspergillusniger, Bacillus cereus, Chlorella Spand also Citrobactersp for removal of dye from industrial wastewater. The adaptability and the activity of each microorganism are the most significant factors that
influence the effectiveness of microbial activity in the decolorization [78, 79]. Biological treatment is used as a means of removing color, but since most dyes are designed to resist light and oxidation degradation, they are normally less likely to be treated with conventional aerobic therapy. The removal of water-soluble dyes by aerobic processes is a particular problem. Some of these dyes are adsorbed on wastewater sludge [80]. Direct biological treatment can also be used through the use of bacteria or fungi, but the nutritional and physiological requirements of microorganisms limit the applicability of these bioremediation processes. Research on effective and green oxidation techniques has led to increased interest in the use of enzymes to replace traditional non-biological methods [81]. Biological treatment methods have been effective in reducing of dyehouse effluents, and when properly used, the cost of operation is lower than other treatments. Combinations of chemical and biological or physical and biological treatment have also proven to be effective [82, 83]. Biological treatment of textile azo dyes has been demonstrated to be effective due to its capability for degrading all dye stuff and also overcome many disadvantages posed by the physicochemical processes [84]. Microbes and their enzymes can degrade dye by both aerobic and anaerobic metabolism. There are several reports on the degradation of environmental contaminants by various bacteria. Many of the bacteria are recognized to use exclusively on hydrocarbons. Bacteria with the hydrocarbon-degradation bacteria have the potential for hydrocarbon degradation [85, 86]. These bacterial bioflocculants offer an economical and clean alternative for replacing or supplementing current treatment processes to remove dyes from wastewater effluents, as they are biodegradable and easy to sustain [87]. Locally isolated strains Ps. aeruginosa, Ps. putida and B. cereus explained high decolorization and degradation activities of textile dyes and wastewater effluents [88, 89]. Algae were studied in the field of decolourization of industrial wastewater effluents. Algae are everywhere naturally and be one of the biomaterials with high capacity for dye removal from polluted water because it is photosynthetic organisms distributed almost all over the world and in all habitat types [90]. Fungal cells are an inexpensive and easily available source of biomass that has great potential for dye decolourization, and is therefore an important promising material for the dyes removal from textile wastewater [91]. Enzymes have been used in many fields primarily for their immense catalytic potential. In wastewater treatment, enzymes can be applied for developing of processes of remediation that are less aggressive on environment than traditional treatment. The biological origin of enzymes reduces their adverse impact on the environment thereby making enzymatic wastewater treatment an ecologically sustainable technique. Enzymes from various sources (fungus and plant based) have been applied for the treatment of dye based compounds [92, 93].

5-Membrane technology

The increasing trend of industrialization around the world has led to the generation of industrial effluents in large quantities, containing toxic organic substances, as well as large quantities of suspended materials [94, 95]. Membranes are widely used in different industries of separation processes because of their ability to control materials passing through the membrane, thus achieving a high degree of separation always, making these processes widely acceptable. The membrane is a barrier that allows certain substances to pass through it (permeate) while hindering others (retentate), in a rather specific manner [96]. The significance of membrane technology in wastewater treatment is increasing. Membranes can be used to separate fluids, solids dissolved, suspended or dissolved in colloidal form. The main characteristics of the application of membrane processes in the treatment of consumables are the possibility of removing or recovering valuable or harmful components as well as the possibility of closing water systems, which reduces the consumption of fresh water. The use of
membrane processes enables wastewater to be purified to a degree that is difficult to achieve through using of traditional techniques. The possibility of an application of pressure driven techniques such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) for oily wastewater treatment, has been presented [97]. Membrane technology offers a realistic solution to meet increasingly discharge limits and to reuse textile wastewater by providing treated water with good quality [98]. Membrane technology has been used in treating secondary and tertiary municipal wastewater and oil field produced water [99]. Membranes play an importance role in any advanced dye wastewater treatment system. Prevention of membrane fouling in these advanced membrane separation processes is considered as a critical challenge for ensuring their economic viability [100]. Membrane technology display many applications at different stages of textile processing. These applications are unique because they provide a return on investment while abating the water pollution problem. The main stages of textile processing where membrane technology can be helpful are printing, scouring operations, dyes bath, latex recovery, sizing, and indigo recovery [101]. Many researcher had been studied the role of membrane technology in wastewater treatment especially in textile industry. Nanofiltration is a membrane water treatment technique that find its applications in wastewater and industrial water treatments such as in removal of colorants and organic matters and water softening [102]. Cellulose acetate membrane in reverse osmosis process removed around 90% of color [103]. GO-TiO2 polymer membrane could make considerable improvement in the scope of water and wastewater treatment and could have important effects on the filtration efficiency [104].

6-Electrochemical methods

In recent years electrochemical technologies have been attracted much attention due to the distinctive features of environmental compatibility, safety and versatility. Electrochemical technology compete with other conventional technologies including precipitation, evaporation, ion exchange and solvent extraction to offer solutions to the needs of the different industries [105,106]. Electrochemical technologies been used by researchers for the efficient treatment of wastewater in textile industry [107]. Generally electrochemical technologies are cleaner than physicochemical and membrane technologies especially in color removal from wastewater because it’s using the electron as unique reagent and do not produce solid residues [108,109]. The process is based on the direct degradation of dye on the anode using chloride as electrolyte and on the indirect oxidation of dyes using the generated species [110]. Electrochemistry offers promising methods to prevent pollution problems in the process industry. The feasibility of electrochemical conversion/destruction of organic substrates in wastewater has attracted much attention since pioneering studies to our times [111,112]. The efficiency of electrochemical method based on the nature of the selected anode and stable anodes that are prepared by the precipitation of thin layer of metal oxides on a base metal. Numerous researchers have investigated electrochemical oxidation for degradation of azo dye through optimization of operating parameters using various anodes including RuO2, SnO2, PbO2 and diamond electrode [113]. various advantages of Electrochemical technologies involve high efficiency, easy in operation and handling, automation, simple equipment, safety, operations under ambient temperature and pressure conditions [114]. Electrochemical technologies no need of chemical requirements, occupying a small area in plants and simple operation and not producing any sludge [115]. In addition to the mentioned above its utilization of a green reagent
such as the electron, extremely high removal of multiple contaminants, effective disinfection, high flexibility and no necessity to transport or stock chemical oxidants [116].

**Conclusion**

Wastewater discharged from industries contains large amount of pollutants involving dyes in addition to other pollutants. Removal of dye from textile effluents is an environmental issue which can be fixed by using of textile wastewater treatment. So several chemical, physical and biological methods are reviewed in this paper for dyes removal from industrial wastewater.

**References**


[96] Chollom, M. N. Treatment and reuse of reactive dye effluent from textile industry using membrane technology. MSc Thesis submitted to Durban University of Technology Faculty of Engineering and the Built Environment, Department of Chemical Engineering, pp.1-60, 2014


