Color Removal from Dye Wastewater: A Review

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Abstract - *Dyes are organic compounds which are highly toxic in many aspects and it is advisable to remove them from the environment that they are polluting. The legislation in many countries has become stringent and thus has led to research of new techniques for removal of dyes and their color from dye wastewater. This paper is a review of the existing methods, their advantages and disadvantages. The methods are divided into physio/chemical and biological categories. No one method is able to completely remove color at low cost, high efficiency and at certain conditions. Some methods are specific and can only be applied to certain dyes while others can be applied to a wide range but are more efficient with certain dyes. Thus a more cost effective, efficient and widely applicable method is needed. Perovskite is a catalyst which be used for adsorption of dyes, it can be modified to be dye specific and has low cost. This paper gives a view on certain modifications of perovskite and their ability to remove certain dyes.*

Keywords: *Dyes, removal method, adsorption, perovskite.*

1. INTRODUCTION

Dyes are organic compounds comprising of two main components: chromophores which are accountable for color and auxochromes which are accountable for intensity of dyes. Depending on chromophores, 20–30 different groups of dyes are distinguished, with azo, anthraquinone, phthalocyanine and triarylmethane being the key groups [1]. Dyes are not completely used in the course of manufacturing in the textile industry, and around 2-20% is discharged as effluent thus introducing excessive concentrations of dyes in wastewater. The ETAD 1974 aims to minimize environmental damage, protect users and consumers and to co-operate fully with government and public concerns over the toxicological impact of their products. Furthermore environmental legislation since 1974 has been strict thus resulting in research for methods for dye removal [2].

1.1. Impact

Dyes, having synthetic origin and complex aromatic molecular structures are highly stable thus making biodegradation nearly ineffective. Many organic and inorganic chemical reagents are used in the production of dyes, causing dyes to have direct and indirect toxic effects on humans in the form of tumors, cancers, and allergies. Also dyes inhibit growth at various trophic levels also involving bacteria, algae, protozoans, plants and animals. The presence of dyes in water reduces light penetration and hinders photosynthesis in aquatic plants. Decolorization of waste waters containing dye impurities is also important, as color is prominently visible which affects the water transparency ethics requiring the wastewater to be treated. The color removal process for dye wastes consists of either concentrating the color into sludge or the complete destruction of the dye molecule [1,2].

1.2. Color measurement in colored wastewaters

To measure color the most general methods are by comparing visually and by spectrophotometry, albeit there is no universal method to examine colored wastewater emissions [3].

1.3. Methods for removal of color from dye wastewater

The main removal methods for dyes and dye wastes are physicochemical and biological methods. Physicochemical methods include processes such as membrane filtration, precipitation, flotation,

coagulation/flocculation, adsorption, ion pair extraction, ultrasonic, electrolysis, chemical reduction mineralization, and advanced chemical oxidation. Biological processes involve aerobic, anaerobic, and fusions of the two that can be again divided into suspended and attached growth systems [2]. The color of polluted water with organic colorants, decreases when the cleavage of the -C=C- and the -N=N- bonds and heterocyclic and aromatic rings occurs. The absorption of light by the associated molecules is shifted from the visible to the ultraviolet or infrared region of the electromagnetic spectrum when the degradation of the dye molecule occurs [4].

1.3.1 Chemical methods

Oxidation process

Oxidation is the most used chemical decoloration process because of its simplicity. Chemical methods include use of oxidizing agents such as ozone (O_3), hydrogen peroxide (H_2O_2) and permanganate (MnO_4) to change the chemical composition of compound or group of compounds i.e. dyes. The most common oxidizing agent used is hydrogen peroxide, which being stable in its pure form needs to be activated. Oxidation methods may differ in the way in which hydrogen peroxide is activated [4, 5].

Ozone is recognized widely because of its high reactivity and good removal efficiencies with dyes but it is also been reported that ozone is not efficient with non-soluble disperse and vat dyes which react slowly and take longer reaction time [6]. Its advantage are that it produces a product that is decolorized, has low COD, and which returned to processing or discharged into the environment [2].

Advanced oxidation process (AOP) using an H_2O_2/Ultraviolet (UV) system is an emerging technology for handling large volumes of textile wastewater. Hydroxyl free radicals which are powerful oxidizing species are strongly generated by this system. The AOP decomposes chromophores of the dye giving complete decolorization. No sludge is formed during any stage of this treatment [2]. E.g. Fenton reaction in which hydrogen peroxide is added in an acid solution (pH =2-3) containing Fe^{2+} ions [5].

1.3.2 Physical methods

Coagulation or precipitation processes

In the coagulation process chemicals are dispersed in wastewaters rapidly, thus changing the characteristics of the particles which are suspended in the dye wastewater so that they aggregate to form flocs that settle down rapidly. It is affected by the following factors: chemicals, pH, and temperature of the system [2]. Coagulation is regarded as the most successful pretreatment in wastewater treatment [5]. Its advantage is low capital cost, while its major limitation is the generation of sludge and ineffective decolorization of some soluble dyes [5].

Adsorption

Adsorption can destroy or change the chromophore of the dye so as to remove the color therefore removing the entire dye molecule leaving no fragments in the wastewater. But it does not always remove residual functional groups of dye molecules thus the treated effluent still can cause environmental difficulties. Mostly clay minerals like kaolinite and montmorillonite, and activated carbon are used as adsorbents; however, these materials are expensive and need regeneration. Activated carbon can achieve sharp removal rates (90%) with cationic, mordant and acid dyes. A criterion for adsorbent selection is usually dependent on characteristic such as high affinity, capacity of target compound and the possibility of regeneration of adsorbent [2, 5].

Membrane Process

The membrane process can achieve a distinct decrease in COD, but as the dyes have to be removed from the membrane, there is a major problem of disposal of heavily loaded concentrates. Reverse osmosis, ultrafiltration and nanofiltration are the main filtration techniques used for chemical recovery and treatment of effluent [2, 5].

Ion Exchange

Ion exchange has not been widely used for the treatment of dye-containing effluents, mainly

because this process cannot accommodate a wide range of dyes. Both cation and anion dyes can be removed from dye-containing effluent this way. Advantages of this method include no loss of adsorbent on regeneration, reclamation of solvent after use and the removal of soluble dyes. A major disadvantage is cost. Organic solvents are expensive, and the ion exchange method is not very effective for disperse dyes. One of the effective anion exchangers, gaining in applicability in the recent years, is quaternized cellulose.

1.3.3 Biological Methods

The biological mechanisms can be complex with biodegradation as the major one. This method is economically efficient. Microbes interact with dye molecules by binding to cell surface by hydrophobic, ionic and covalent interactions, interactions with enzymes which modify the redox characteristics of dyes, interactions with enzymes which degrade dyes, transport into the cell and transport of transformed dyes (decomposition or redox-transformed products) out of cells. Many organisms i.e. bacteria: revibacillus sp., Klebsiella pneumoniae, Acetobacter liquefaciens, and Pseudomonas desmolyticum, yeasts, filamentous fungi, etc. are used in dye removal. Dye removal by living cells includes complex mechanisms for example intracellular and extracellular oxidase and biosorption. Living cells are intricately involved with the operating parameters i.e. nutrition necessities, the influent concentration and toxicity. Dead cells use only biosorption- physicochemical interactions i.e. adsorption, deposition and ion-exchange. These cells have the advantages of long storage periods, easy operation, and simple regeneration [2]. A huge number of microbes have been experimented on for decoloration and decomposition of different dyes. Mostly dye molecules are chemically stable and are resilient to microbiological attack. Efficiency of bioremediation can be increased in the near future by isolating new strains and adapting existing strains for the decomposition of dyes. Also efficiency of microbiological degradation can be improved by merging techniques like bioremediation and physicochemical methods [6]. Cells can be trapped in a polymer matrix, covalently bonded to a support matrix, covalently cross-linked from cell to cell, adsorbed onto a solid support, or flocculated. An immobilization matrix in bead form can also be used in packed columns or in a fluidized-bed reactor. The benefits of these reactors include maximum reaction rates, minimum nutrient depletion, and product inhibition, and better mass transfer through a decreased feed viscosity and increased differential velocities.

1.3.4 Combined methods

From the above it can be realized that a universally suitable effluent treatment solution is impracticable therefore a combination of various techniques have to be used as a technical and economical appropriate option. Based on information of conceivable hybrid methods and the available cost information, it can be concluded that biological hybrid technologies appear to be highly encouraging. In these integrated methods, the effectiveness of combining biological and other treatments is specifically designed to be synergetic rather than additive in contrast to the conventional pre- or post-treatment concepts, where process designs of different components are not dependent of one another. Researches performed in the last years involve a biological system following the AOP pre-oxidation effective treatment of real or artificial dye wastewater. For example, applicability of AOPs (ozone, hydrogen peroxide, UV radiation and Fenton's reagent) combined with an aerobic biological treatment were considered [4].

1.4 Advantages and disadvantages of methods

The major considerations for selection of convenient methods for dye wastewater treatment are time required for desired degree of treatment and operating cost. Nonetheless there is no single economically and technically feasible method, thus usually two or more methods have to be combined to accomplish a required level of removal of color [5]. Most methods are non-destructive and just transfer the organic pollutants from water to another phase, thereby causing secondary pollution. Also regeneration of adsorbent materials and post treatment of solid-wastes when needed are expensive

operations. All the methods have their own advantages and disadvantages, therefore their selection will be predicted based on characteristics of wastewater like type and concentration, pH, toxic compounds and salinity. The most common combination is that of biological oxidation and physical- chemical treatment methods [7].

Table 1: Advantages and disadvantages of different methods

Method	Advantages	Disadvantages	Ref.
Fenton's reagent	Effective decolourisation of both soluble & insoluble dyes	Sludge Generation, and its handling, longer treatment time	[5,8]
Ozonation	Applied in gaseous state, does not increase volume of wastewater & sludge, occurs in relatively short time	Short half-life (20 min), high cost, good colour removal but not significant COD reduction	[5,8]
Photochemical	No sludge production	Formation of by-products, colour and COD reduction is not very significant	[8]
NaOCl	Initiates and accelerates azo-bond cleavage	Release of carcinogenic aromatic amines & toxic compounds	[8]
Cucurbituril	Good sorption capacity for various dyes	High cost	[8]
Electrochemical Destruction	Breakdown compounds are non-hazardous	High cost of electricity	[3,8]
Ion exchange	Regeneration; no adsorbent loss, efficient recovery of dyes	Not effective for all dyes, high cost for regeneration, dye specific	[8]
Membrane filtration	Removes all dye types	Concentrated sludge production, high cost	[5,8]
Irradiation	Effective oxidation at lab scale	Requires a lot of dissolved O_2	[8]
Electrokinetic coagulation	Economically feasible	High sludge production	[8]
Adsorption	Excellent removal of wide variety of dyes, strong binding with organic substances	Regeneration difficulties, costly disposal of adsorbents	[3,5]
Sonolysis	No extra sludge production	Requires a lot of dissolved oxygen, high cost	[5]
Electro-coagulation	Good removal of dye	High cost, less electrode reliability	[5]
Biological Process	Environment friendly	Slow process, need of adequate nutrients, narrow operating temperature range, degree of aromatics present in dye molecules and the stability of modern dyes present a problem	[7,5]
Chemical coagulation & flocculation	Economically feasible, excellent colour removal	Sludge production	[5]
Oxidation	Rapid process	High energy costs and formation of by-products	[9]
Bioreactors	Combination of biological and chemical/ physical methods, attractive technology	Ways to immobilize redox mediators in bioreactors is a challenge	[7]

2. Use of adsorption method

Various adsorbents such as clays, activated carbons, silica, biomass, compost, sludge, plant or lignocellulosic wastes, peat, biopolymers, etc. have been used to remove different types of dyes from wastewaters. The physical characteristics of the adsorbents, such as, surface area, porosity, size distribution, density and surface charge have high influence in the adsorption process. As a result, there has been a great interest in developing new adsorbent materials with diverse compositions, properties and functionalities.

Table 2: Advantages and disadvantages of different adsorbent

Adsorbent Used	Advantages	Disadvantages	Ref.
Activated Carbon	Good removal of variety of dyes	Very expensive	[8]
Bagasse Pith			
Banana and Orange Peel	Low cost ,effective	Not as effective as activated carbon	[10]
Bone Char			
Peat	Inexpensive, widely available		[11]
Alumina			
Silica Gel	Effective for basic dye removal, adsorption capacities were high	Side reactions prevent commercial application, expensive	[8,12]
Lignite			
Coal		Short time	[12]
Chitin	Abundant in nature, low cost	Efficient for cationic dyes	[11]
Chitosan			
Zeolite	Selective adsorbent, effective	Expensive	[12]
Sludge			
Diatomite	High selectivity for basic and reactive dyes	pH dependent	[13,12]
Dolomite			
Fungus			
Peat	Good adsorbent due to cellular structure, disposable by burning	Specific surface area for adsorption are lower than activated carbon	[8,12]
Wood chips	Good sorption capacity for acid dyes, low cost, can be regenerated, can be disposed by burning and using heat energy	Requires long retention time	[8]
Biomass	Low cost	Slow, pH dependent, clogging if used in column	[12]
Clay	Low cost, large surface area, properties can be modified	Dependent on pH, temperature	

3. Perovskite as a unique adsorbent for treatment

The general formula for the family of perovskite-type oxides is ABO_3 (where A and B represent a rare earth metal with large ionic radius or alkali earth metals and a transition metal with a small ionic radius respectively). The perovskite family can be evaluated as adsorbent materials or catalysts for removal of dyes [1]. Distorted perovskites have reduced symmetry, which is important for their magnetic and electric properties. The perovskite

structure is known to be very flexible and the A and B ions can be varied leading to the large number of known compounds with perovskite or related structures.

E.g. Perovskites, e.g. titanium or niobium perovskites, $BaTiO_3$ and $LiNbO_3$, have been intensively studied in the past as high dielectric permittivity or ferroelectric materials. Perovskite-phase metal oxides exhibit a variety of interesting physical properties which include ferroelectric, dielectric, pyroelectric, and piezoelectric behavior. Perovskite-type oxides with typically very high melting points also exhibit a number of interesting chemical properties including heterogeneous catalytic activity. For example, these oxides are often utilized for CO oxidation, oxidation of hydrocarbons and chlorinated volatile organic compounds, partial oxidation of methane to synthesis gas, N_2O decomposition, NO_x reduction, hydrogenation reactions of alkenes, SO_2 reduction, as well as in various types of electro- and photocatalytic reactions.

Due to their unique perovskite structure and the properties, the perovskite photocatalyst family (which include ABO_3, double perovskites $A_2B'B''O_6$ and a typical Lanthanum-based pervoskite-type $La_2Ti_2O_7$ (a layered perovskite)) were found to be alternative visible-light photocatalytic active photocatalysts for water splitting and pollutant degradation [13].

Many articles have examined the effectiveness of spinel-type oxides as catalysts for removal and photo-degradation of water-soluble dyes, but the degradation pathway for the removal of azo dyes from aqueous solutions, and the confirmation and optimization of the efficiencies of the perovskite oxide catalysts have acquired very little scrutiny in literature [1].

Table 3: Use of perovskite catalysts for removal of dyes

Perovskite	Techniques used	Preparation method	Pollutants	Methods used to remove pollutants	Operating condition	Result	Ref.
$SrFeO_{3-\delta}$	XRD, SEM, BET and zeta Potential analyses	High temperature, high energy ball milling process	Bisphenol A (BPA),an azo dye, Acid Orange 8 (AO8)	Degradation	-	Complete decolourization of A08, 83% TOC removal BPA	[15]
$La_{0.5}Ca_{0.5}NiO_3$	DTA/TGA, XRD, TEM,STM, SEM, EDX	Sol-Gel method	Reactive blue 5	-	Catalytic dosage of 0.03 g, pH=2	100% removal of RB5	[1]
$BiAg_xO_y$	XRD, FTIR, TEM, EDX, XPS	Coprecipitation	Rhodamine B (Rh B)	Degradation, oxidative, Decomposition	-	-	[16]
$LiCo_{0.5}Fe_{0.5}O_2$	DTA, Far-IR, XRD, STM, SEM and TEM	Sol-gel method	Reactive blue 5	-	pH=1	-	[17]
Cu-dope $LaTiO_3$	XRD, X-ray photoelectron spectroscopy	Sol–gel method	Rhodamine B	Enhanced Fenton degradation	Catalytic dosage of 0.07 g, pH=4-9	High activity for the decolorization and mineralization of RhB	[18]
$LaFe_{0.9}Cu_{0.1}O_3$	XPS, ICP-OES, XRD	Citrate method	Oxalic acid, Reactive Blue 5	Catalytic Ozonation	-	TOC removal close to 100% after 3 h	[19]
Co substituted $BiFeO_3$ ($BiFe_{0.95}Co_{0.05}O_3$)	XRD, Raman, and PPMS	Complex sol–gel method	Rhodamine B	Electrostatic interaction, sorption,	-	-	[20]
$La_{0.7}Sr_{0.3}MnO_3$	XRD, TEM, FTIR	Combination of ultrasound and co-precipitation method	P-chlorophenol	Sono-catalytic degradation and fast mineralization	Catalytic dosage of 0.07 g	88% decrease in the concentration and 85% decrease in the TOC for 4-chlorophenol	[21]

$SrTi_{0.9}Zr_{0.1}O_3$	TG–DTA, XRD, UV, SEM–EDX, TEM–EDX, TPR	Sol–gel process	Acid black (AB)	Photocatalytic degradation	-	-	[22]
$KMgF_3$	XRD, TEM, XPS, UV–vis DRS	Microemulsion and sol–gel methods	Rhodamine B, methyl orange, phenol and chlorophenol	Degradation	-	Rh B 98%, MO 91%, phenol 86%, chlorophenol 89%	[14]
$LaTi_{0.15}Cu_{0.85}O_3$	N_2, Hg Adsorption, XRD, SEM, TEM, FTIR, TG, DTA, TPR	Citrate method	Gallic acid (used in preparation of dyes)	Ozonation	Catalyst dosage of 2.5 g/L	TOC Reduction > 90%	[23]
$LaFeO_3$ $LaCoO_3$ (better activity than Mn-based)	-	Sol-Gel method RG	Salicylic acid	-	-	-	[24]
$NaTaO_3$ doped with 1M% La,Sm	XRD, SEM, IR, N_2 Adsorption	Sol-Gel, Solid State Reaction	Methylene Blue	Photocatalysis	150 mg dose in 250 ml of 300 ppm MB 1h time UV light	Sm doped SG at 600°C has 4 times SSA than La doped	[25]
$BaTiO_3$	SEM, XRD, HR-XPS, FTIR, DR-UV, BET	Hydrothermal reaction	Crystal Violet	Photocatalytic degradation		99% degradation with 130°C 48h prepared catalyst	[26]
Y_2InSbO_7 (better activity) and Y_2GdSbO_7	XRD, SEM, XFS, XPS, BET, TEM	Solid State Reaction	Rhodamine B	Photocatalytic degradation, continuous mineralization		Complete removal at 220 & 235 min resp. Reduction of TOC and evolution of CO_2	[27]
KNb_3O_8	SEM, XRD	Solid State Reaction	Acid Red G	Photocatalysis under UV irradiation	1.0 g/L	100% removal at 60 min	[28]
$SrTiO_3/CeO_2$ composite			C.I. Direct Red 23	Photocatalytic degradation under UV irradiation	1.5 g/L pH=12	100% decolorisation at 60 min, COD removal of 69% at 240 min	[29]
$MgAl_2O_4$	XRD, SEM, TEM, EDX, TG, DRS, BET, XPS, FTIR	Simple Solution Combustion Method	MB	Photocatalytic degradation under visible irradiation		99.5% MB degradation in 100 min	[30]

4. Conclusion

The dye-containing industrial wastewaters discharged into streams and river constitutes one of the major sources of water pollution. Color waters are objectionable on aesthetic grounds for drinking and other agricultural purposes. In addition, some dyes are either toxic or mutagenic and carcinogenic. So, these wastes must be treated prior to discharge in order to comply with the environmental protection laws for the receiving waters. The various treatment technologies recommended meeting color removal requirements are physical-chemical treatment operations including adsorption, ozonation and chemical precipitation. Each has its merits and limitations in application. The adsorption process is attractive alternative treatment process and perovskites are used as inexpensive adsorbent over

other conventional adsorbents and remove color efficiently.

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