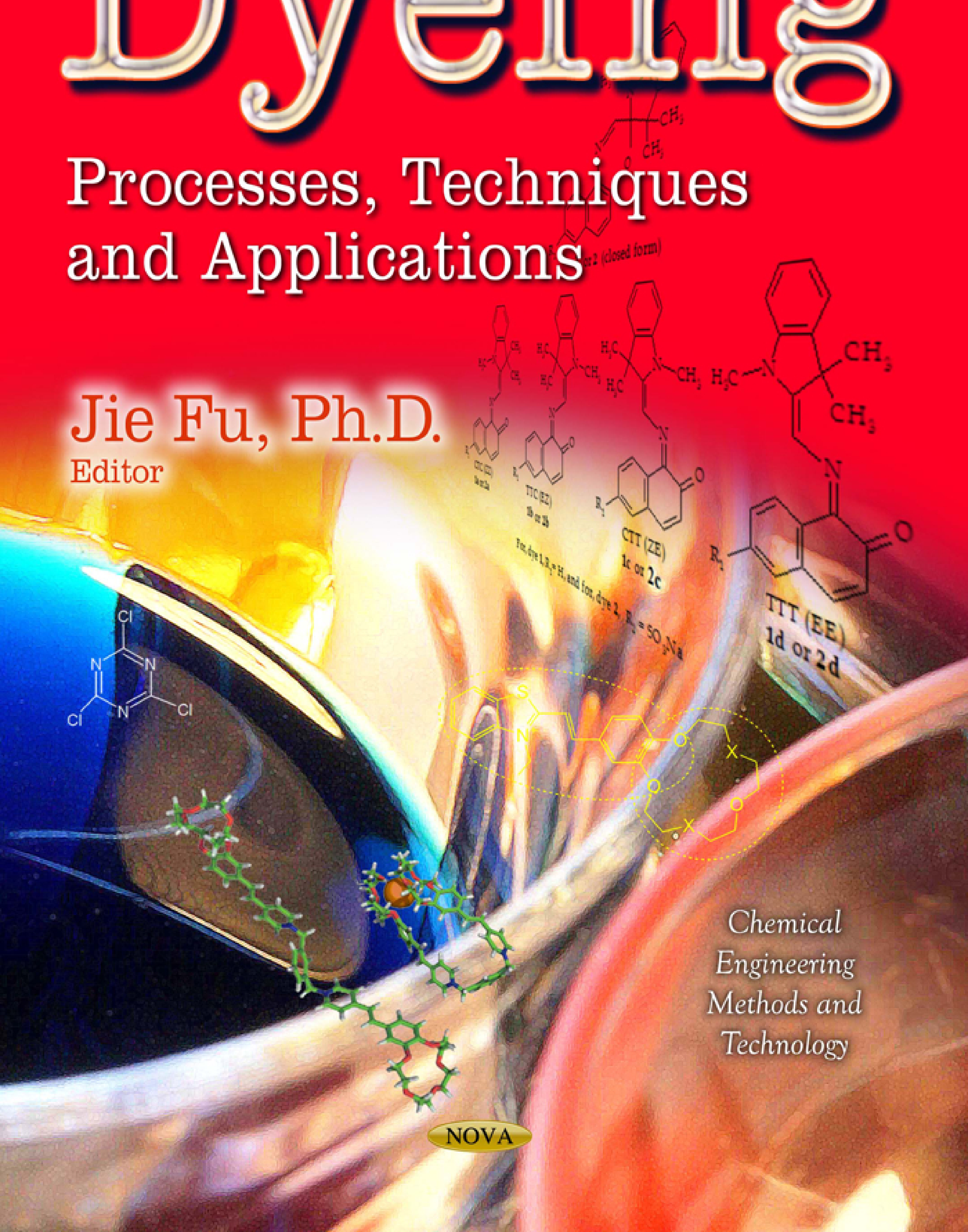
Dyeing

Processes, Techniques and Applications

Jie Fu, Ph.D.
Editor



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JIE FU
EDITOR

nova publishers
New York

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Additional color graphics may be available in the e-book version of this book.

Library of Congress Cataloging-in-Publication Data

Dyeing : processes, techniques, and applications / editor, Jie Fu (School of the Environment, Nanjing University, Nanjing, China).
pages cm
Includes bibliographical references and index.
ISBN: 978-1-62808-871-7 (eBook)
1. Dyes and dyeing. I. Fu, Jie, 1982- editor of compilation.
TP897.D788 2013
667'.2--dc23
2013031598

Published by Nova Science Publishers, Inc. † New York

CONTENTS

PREFACE

The art of color application to enhance our self appearance and decorate the world around us has been known to man for many centuries. Historical records indicate the use of natural dyes extracted from vegetables, fruits, flowers, insects and fish date back to 3500 BC. Color is the one of the main attractions of any fabric; an unsuitable color choice can make commercial products unsuccessful. Fabrics were dyed earlier with natural dyes, however these natural dyes gave a dull, limited range of colors. The discovery of synthetic dyes by W. H. Perkins in 1856 has provided a wide array of dyes with a wider color range and brighter shades, and as a result, “dyeing” has become a massive industry today.

Currently, a large number of synthetic dyes are produced worldwide every year, and a portion of them are discharged with wastewater. Due to the toxicity and potential carcinogenicity, the removal of such dyes has become an important environmental issue. However, besides the dyestuff, there are some slurries, dyeing aids, acids or alkalis, fibers and inorganic compounds in dyeing wastewater, all of which aid in the characterization of dyeing wastewater by its strong color, high pH, high chemical oxygen demand, and its low biodegradability. Thus, dyeing wastewater is difficult to treat, and has become a big challenge for mankind.

In order to introduce the knowledge of the above two aspects and discuss the advances, *Dyeing: Processes, Techniques and Applications* has been prepared; its contents focus on the application of various dyes in the dyeing process and treatment of dyeing wastewater. The applied dyes include not only synthetic dyes (reactive dye and photochromic dye) but also natural dyes (indigo and treat bark extract). The concerned technologies for the treatment of dyeing wastewater cover adsorption, electrochemical technique, coagulation/flocculation, biological treatments, and membrane bioreactors. Besides these contents, salt-free dyeing auxiliaries and hollow filament fabrics are also discussed.

This book has rich and extensive contents and it is suitable for both researchers and general readers. There are many general descriptions for some kinds of dyes and dyeing wastewater treatment technologies. From these contents, the readers can get a comprehensive understanding on the stuff or technology. Some state-of-the-art techniques are also introduced and readers can collect useful information on the current advances and developing trends.

The authors of this book are scientists or engineers from prominent institutes and universities around the world. They have multiple experiences and professional knowledge in related areas, and it has been a great honor for me to work with them. I would like to thank Roshan Paul (Hohenstein Institut für Textilinnovation gGmbH), Shah M. Reduwan Billah

(Durham University), Olga Fedorova (A. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences), Lijing Wang (RMIT University – Melbourne), Nizar Meksi (Monastir University), Rattanaphol Mongkholrattanasit (Rajamangala University of Technology PhraNakhon), Seung Jin Kim (Yeungnam University), George Z. Kyzas (Technological Educational Institute of Kavala), Víctor López-Grimau (Universitat Politècnica de Catalunya), Abu Zahrim Yaser (Universiti Malaysia Sabah), Xiaobai Zhou (Nanjing University), and Carmen Gutiérrez-Bouzán (Universitat Politècnica de Catalunya-Barcelona Tech). Without your cooperation and hard work, the completion of *Dyeing: Processes, Techniques and Applications* wouldn't have been possible.

Jie Fu
Jun 26, 2013, In Auburn, AL, USA

In: Dyeing: Processes, Techniques and Applications
Editor: Jie Fu

ISBN: 978-1-62808-847-2

Chapter 9

ADSORPTION AS THE MOST PROMISING DECOLORIZATION TECHNIQUE IN THE FINAL STEP OF TEXTILE EFFLUENTS TREATMENT

George Z. Kyzas[1,2,*]
[1]Department of Petroleum and Natural Gas Technology, Technological Educational Institute of Kavala, Kavala, Greece
[2]Laboratory of General & Inorganic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece

ABSTRACT

Wastewater discharged from the dye–houses can be one of the biggest contributors to aquatic pollution. The most studied dye classes, in the dye bearing effluent treatment, are reactive and basic. The dye loss from the dyeing process to the effluent is estimated 10–50% for reactive dyes and 0–5% for basic ones. Given that reactive and basic dyes could simultaneously exist in the equalization tank of a dye–house, it is of fundamental importance to remove both of them. The dyeing process of cotton textiles using reactive dyes (cotton fibers makes up about half of the worldwide consumption of fibers) involves unit operations such as (i) desizing, (ii) scouring, (iii) bleaching, (iv) dyeing, and (v) finishing. The waste streams from each individual sub–operation are collected to an "equalization tank", where they are mixed and homogenized. So, the large volume of colorized effluents after the dyeing process has to be treated in some manner. A typical effluent treatment is broadly classified into preliminary, primary, secondary, and tertiary stages. The preliminary stage includes equalization and neutralization. The primary stage involves screening, sedimentation, flotation, and flocculation. The secondary stage reduces the organic load and facilitates the physical/chemical separation (biological oxidation). The tertiary stage is focused on decolorization, which is the main problem. In the latter, adsorption is characterized as a promising decolorization technique. Adsorption onto activated carbon is broadly used to limit the concentration of color in effluents. Adsorption has been applied either in a single mode, mainly for dyes removal from

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[*] Corresponding author: St. Lucas University Campus, Technological Educational Institute of Kavala, Kavala 65404, Greece.Email: georgekyzas@gmail.com; drkyzas@chem.auth.gr; kyzas@teikav.edu.gr.

simulated/synthetic wastewaters, or in a combinational mode for total cleaning of real wastewaters. Recently, other materials, more economical, have been attempted to be used as adsorbents at the tertiary stage of effluent's treatment replacing the activated carbon: natural materials, biosorbents, waste materials from industry and agriculture), clay materials (bentonite, kaolinite), zeolites, siliceous material (silica beads, alunite, perlite), agricultural wastes (bagasse pith, maize cob, rice husk, coconut shell), industrial waste products (waste carbon slurries, metal hydroxide sludge, coffee wastes), biosorbents (chitosan, peat, biomass) and others (starch, cyclodextrin, cotton). The present chapter focuses on the challenge of adsorption as the last technique in the chain of treatment of dyeing effluents, presenting various advantages versus other techniques (reverse osmosis, ozonation etc).

Keywords: Decolorization, textile effluents, adsorption, low–cost materials, bacterials, activated carbon, chitosan

INTRODUCTION

Wastewater discharged from dye–houses can be one of the biggest contributors to aquatic pollution. The most studied dye classes, in the dye bearing effluent treatment, are reactive and basic [1–3]. The dye loss from the dyeing process to the effluent is estimated 10–50% for reactive dyes and 0–5% for basic ones [4]. Given that reactive and basic dyes could simultaneously exist in the equalization tank of a dye–house, it is of fundamental importance to remove both of them [5].

The dyeing process of cotton textiles using reactive dyes (cotton fibers makes up about half of the worldwide consumption of fibers) involves unit operations such as (i) desizing, (ii) scouring, (iii) bleaching, (iv) dyeing, and (v) finishing [6, 7]. The waste streams from each individual sub–operation are collected to an "equalization tank", where they are mixed and homogenized. In particular, the wastewater produced by the dyeing bath–reactor contains hydrolyzed reactive dyes, dyeing auxiliaries, electrolytes (~ 60–100 g/L of NaCl and Na2CO3). The latter are responsible for the high saline content of the wastewater, which exhibits high pH values (10–11) [7]. In a typical dyeing procedure with reactive dyes, for 1 kg of cotton are required 0.6–0.8 kg of NaCl, 30–60 g of dyestuff, and 70–150 L of water [7]. So, the large volume of colorized effluents after the dyeing process has to be treated in some manner.

The research on textile effluent decolorization has been often focused on reactive dyes for three main reasons: (i) reactive dyes represent an increasing market share, because they are used to dye cotton fibers, which makes up about half of the world's fiber consumption; (ii) a large fraction, typically around 30% of the applied reactive dyes, is wasted due to the dye hydrolysis in alkaline dye bath; (iii) conventional wastewater treatment plants have a low removal efficiency for reactive and other anionic soluble dyes, which leads to colored waterways [2, 7].

A typical effluent treatment is broadly classified into preliminary, primary, secondary, and tertiary stages [6–8]. The preliminary stage includes equalization and neutralization [6–8]. The primary stage involves screening, sedimentation, flotation, and flocculation. The secondary stage reduces the organic load and facilitates the physical/chemical separation (biological oxidation) [6–8]. The tertiary stage is focused on decolorization[6–9], which is the main problem. In the latter, adsorption is characterized as a promising decolorization technique. Adsorption onto activated carbon is broadly used to limit the concentration of color in effluents [10]. Adsorption has been applied either in a single mode, mainly for dyes removal from simulated/synthetic wastewaters, or in a combinational mode for total cleaning of real wastewaters. Recently, other materials, more economical, have been attempted to be used as adsorbents at the tertiary stage of effluent's treatment replacing the activated carbon: natural materials, biosorbents, waste materials from industry and agriculture), clay materials (bentonite, kaolinite), zeolites, siliceous material (silica beads, alunite, perlite), agricultural wastes (bagasse pith, maize cob, rice husk, coconut shell) [11–13], industrial waste products (waste carbon slurries, metal hydroxide sludge, coffee wastes) [11, 14–16], biosorbents (chitosan, peat, biomass) and others (starch, cyclodextrin, cotton) [11, 17].

The present chapter focuses on the challenge of adsorption as the last technique in the chain of treatment of textile effluents, presenting various advantages versus other techniques (reverse osmosis, ozonationetc).

TEXTILE EFFLUENTS

On the basis of waste and wastewater (or effluent) generation, the textile mills can be classified into two main groups namely dry processing mills and wet processing mills [18]. In the dry processing mills, mainly solid waste is generated due to the rejects of cotton. In the other group, desizing, scouring, bleaching, mercerizing, dyeing, printing, and finishing are the main processing stages. The wastewater generated by textile industry includes cleaning wastewater, process wastewater, noncontact cooling wastewater, and storm water. The amount of water used varies widely in this industry, depending on the specific processes operated at the mill, the equipment used, and the prevailing philosophy of water use. On account of the involved complexity of different processes at different stages, textile wastewater typically contains a complex mixture of chemicals. Apart from this, large numbers of associated hazards have also been reported by the various chemicals used in different stages of textile processing [19].

Wet processing operations (including preparation, dyeing, and finishing) generate the majority of textile wastewater having very high COD, BOD, TDS and very deep color. Large numbers of chemical constituents such as alkali, acids, bleaching chemicals, enzymes, starch, dyes, resins, solvents, waxes, oils etc. are used in the various steps during textile processing and finally comes out in the effluent after its consumption. Desizing, or the process of removing size chemicals from textiles, is one of the industry's largest sources of wastewater pollutants [20, 21]. In this process, large amount of size chemicals used in weaving processes are discarded. Dyeing operation generates a large portion of the industry's total wastewater. The primary source of wastewater in dyeing operations is spent dye bath and wash water. Such wastewater typically contains by–products, residual dyes, and auxiliary chemicals. Additional pollutants include cleaning solvents, such as oxalic acid. Of the 700,000 tons of dyes produced annually worldwide [22–24], about 10–15% of the dyes are disposed off in effluent from dyeing operations [25, 26].

Dyes in wastewater may be chemically bound to fabric fibers. Dyeing and rinsing processes for disperse dyeing generate about 91–129 m^3 of wastewater per ton of product

[27]. Similar processes for reactive and direct dyeing generate even more wastewater, about 113–151 m^3 per ton of product [24, 27, 28]. This can be attributed to the higher percentage of fixation to the fiber for disperse dyes than acid or reactive dyes. Finishing processes typically generate wastewater containing natural and synthetic polymers and a range of other potentially toxic substances [27]. Textile industries typically generate 200–350 m3 of wastewater per ton of finished product [29, 30] resulting in an average pollution of 100 kg COD per ton of fabric [31].

Raw textile wastewater can be characterized by measurement of BOD, COD, color, suspended solids (SS), dissolved solids (DS) and heavy metals etc. Typical characteristics of textile industry wastewater generally include a wide range of pH, COD, dissolved solids and strong color [32–35], which may be comparable to moderate municipal wastewater [36]. However, the main challenge is to eliminate the color of wastewater, which is due to the remaining dyes. The major characteristics of real textile wastewater have been described in the Table 1.

It has been observed from the Table 1, that the textile wastewaters exhibit wide range of pH from 2 to 14, COD from 50 mg/L to approximately 18,000 mg/L, TDS from 50 mg/L to over 6,000 mg/L and very strong color. This wide variation in the characteristics of textile wastewater is due to complexity of materials used in the textile industry during the processing of textiles.

Textile wastewaters generated from different stages of textile processing contains huge amount of pollutants that are very harmful to the environment if released without proper treatment. The release of textile wastewater to the environment causes aesthetic problems as the changed color of the water bodies such as lakes and rivers, after releasing of wastewater from the industry, cannot be tolerated by the local people. Also, the accumulation of color hinders sunlight penetration, disturbs the ecosystem of receiving water [47, 49, 50]. Ground water systems are also get affected by these pollutants due to leaching through the soil [51, 52]. Apart from this, several dyes and their decomposition derivatives have proved toxic to aquatic life (aquatic plants, microorganisms, fish and mammals) [48, 50, 53]. Additionally, fairly intensive studies has inferred that such colored allergens may undergo chemical and biological assimilations, cause eutrophication, consume dissolved oxygen, prevent re–oxygenation in receiving streams and have a tendency to sequester metal ions accelerating genotoxicity and microtoxicity[54, 55]. In a wider sense, sporadic and excessive exposure to colored effluents is susceptible to a broad spectrum of immune suppression, respiratory, circulatory, central nervous and neurobehavioral disorders presage as allergy, autoimmune diseases, multiple myeloma, leukemia, vomiting, hyperventilation, insomnia, profuse diarrhea, salivation, cyanosis, jaundice, quadriplegia, tissue necrosis, eye (or skin) infections, irritation to even lung edema [54, 55].

DYES

The first synthetic dye, Mauveine was discovered by the Englishman, William Henry Perkin by chance in 1856. Since then the dyestuffs industry has matured [56]. A dye or dyestuff is a colored compound that can be applied on a substrate. With few exceptions, all synthetic dyes are aromatic organic compounds. A substrate is the material to which a colorant is applied by one of the various processes of dyeing, printing, surface coating, and so on. Generally, the substrate includes textile fibers, polymers, foodstuffs, oils, leather, and many other similar materials [57].

Not all colored compounds are dyestuffs because a colored compound may not have suitable application on a substrate. For example, a chemical such as copper sulphate, which is colored, finds no application on any substrate. If it is applied on a substrate, it will not have retaining power on the substrate and for this reason copper sulphate cannot be termed as a dye. On the other hand, congo red, a typical organic colored compound. When it applied to cotton under suitable conditions can be retained on this natural fiber and due to this finds useful application on this fiber. It is termed as a dyestuff [57].

In the field of chemistry, chromophores and auxochromes are the major component element of dye molecule. Dyes contain an unsaturated group basically responsible for color and designated it as chromophore (“chroma” means color and “phore” means bearer) (Table 2). Auxochromes (“Auxo” means augment) are the characteristic groups which intensify color and/or improve the dye affinity to substrate [57] (Table 2).

To further examine the interactions between dyes and substrates, the classification of dyes is required. It is very important to know the chemistry of the dyes in dyeing effluents, in order to synthesize a suitable adsorbent with the appropriate functional group. Hunger et al [56] mentioned that dyes are classified in two methods. The main classification is related to the chemical structure of dyes and particularly considering the chromophoric structure presented in dye molecules. Another type of classification is based on their usage or applying. The classification of dyes by usage or application is the most important system adopted by the Color Index (CI). Aside from mentioned above, there are azoic dyes, ingrain dyes, pigment [56, 57]. Comparative analysis of dye classes are presented in Table 3.

Table 1. The major characteristics of real textile wastewaters

pH	COD (mg/L)	BOD_5 (mg/L)	TSS (mg/L)	TDS (mg/L)	Ref
8.8–9.4	595±131	379±110	276±76	–	[34]
11.2	2276	660	–	47.9	[37]
5–10	1100–4600	110–180	–	50	[21]
6.5–8.5	550–1000	–	100–400	–	[32]
2.7	7000	–	440	930	[38]
13.56	2968	–	–	–	[39]
12–14	1500–2000	–	–	–	[29]
10	1150	170	150	–	[40]
9	750	160	–	–	[41]
2–10	50–5000	200–300	50–500	–	[35]
8.32–9.50	278–736	137	85–354	1715–6106	[42]
8.7	17900±100	5500±100	23900±50	1200±50	[43]
9.30	3900	–	–	–	[44]
7.8	810±50	188±15.2	64±8.5	–	[45]
13	2300±400	–	300±100	–	[33]
6.95	3422	–	1112	–	[46]
7.86	340	210	300	–	[47]
7.5	131±18	–	75±13	1885±80	[48]

Table 2. Names of chromophore and auxochrome groups of dyes

Chromophore group	Name	Auxogroup	Name
$-N=N-$	azo	$-NH_2$	amino
$-N=N^+-O^-$	azoxy	$-NHCH_3$	methyl amino
$-N=N-NH$	azoamino	$-N(CH_3)_2$	dimethyl amino
$-N=O$, $N-OH$	nitroso	$-SO_3H$	sulphonic acid
$>C=O$	carbonyl	$-OH$	hydroxy
$>C=C<$	ethenyl	$-COOH$	carboxylic acid
$>C=S$	thio	$-Cl$	chloro
$-NO_2$	nitro	$-CH_3$	methyl
$>C=NH$, $>C=N-$	azomethine	$-OCH_3$	methoxy
		$-CN$	cyano
		$-COCH_3$	acetyl
		$-CONH_2$	amido

Table 3. Classification of dyes and their properties

Class	Fiber type	Chemistry	Characteristics
Acid	nylon, wool, silk, paper ink, leather	azo, anthraquinone, azine, nitro, nitroso	• anionic compounds • highly water soluble • poor wet fastness
Azoic	cotton, rayon, cellulose acetate, polyester	azo	• contain azo group • metallic compounds
Basic	leather, wool, modified nylon, polyacrylonitrile, polyester, inks	cyanine, azo, azine, triarylmethane, acridine, oxazine, anthraquinone	• cationic • highly water soluble
Direct	cotton, paper, rayon, leather, nylon	azo, phthalocyanine, nitro, benzodifuranone	• anionic compounds • highly water soluble • poor wet fastness
Disperse	polyester, polyamide, acetate, acrylic	azo, anthraquinone, styryl, benzodifuranone	• colloidal dispersion • low water solubility • good wet fastness
Mordant	wool, leather, anodized aluminium	azo, anthraquinone	• anionic compounds • water soluble • good wet fastness
Reactive	cotton, wool, silk, nylon	azo, anthraquinone, phthalocyanine, formazan	• anionic compounds • highly water soluble • good wet fastness

DECOLORIZATION TECHNIQUES

Methods of dye wastewater treatment have been reported [58–61]. Also, fungal and bacterial decolorization methods have been reviewed [62–65]. There are several reported methods for the removal of pollutants from effluents. The technologies can be divided into three categories: biological, chemical and physical [58]. All of them have advantages and drawbacks. Because of the high cost and disposal problems, many of these conventional methods for treating dye wastewater have not been widely applied at large scale in the textile and paper industries. At the present time, there is no single process capable of adequate treatment, mainly due to the complex nature of the effluents [66, 67]. In practice, a combination of different processes is often used to achieve the desired water quality in the most economical way. A literature survey shows that research has been and continues to be conducted in the areas of combined adsorption–biological treatments in order to improve the biodegradation of dyestuffs and minimize the sludge production.

Biological treatment is often the most economical alternative when compared with other physical and chemical processes. Biodegradation methods such as fungal decolorization, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents because many microorganisms such as bacteria, yeasts, algae and fungi are able to accumulate and degrade different pollutants [61, 63, 64]. However, their application is often restricted because of technical constraints. Biological treatment requires a large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation [68]. Biological treatment is incapable of obtaining satisfactory color elimination with current conventional biodegradation processes [58]. Moreover, although many organic molecules are degraded, many others are recalcitrant due to their complex chemical structure and synthetic organic origin [69]. In particular, due to their xenobiotic nature, azo dyes are not totally degraded.

Chemical methods include coagulation or flocculation combined with flotation and filtration, precipitation–flocculation with Fe(II)/$Ca(OH)_2$, electroflotation, electrokinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes. These chemical techniques are often expensive, and although the dyes are removed, accumulation of concentrated sludge creates a disposal problem. There is also the possibility that a secondary pollution problem will arise because of excessive chemical use. Recently, other emerging techniques, known as advanced oxidation processes, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for pollutant degradation. Although these methods are efficient for the treatment of waters contaminated with pollutants, they are very costly and commercially unattractive. The high electrical energy demand and the consumption of chemical reagents are common problems.

Different physical methods are also widely used, such as membrane–filtration processes (nanofiltration, reverse osmosis, electrodialysis) and adsorption techniques. The major disadvantage of the membrane processes is that they have a limited lifetime before membrane fouling occurs and the cost of periodic replacement must thus be included in any analysis of their economic viability. In accordance with the very abundant literature data, liquid–phase adsorption is one of the most popular methods for the removal of pollutants from wastewater since proper design of the adsorption process will produce a high–quality treated effluent. This process provides an attractive alternative for the treatment of contaminated waters, especially if the adsorbent is inexpensive and does not require an additional pre–treatment step before its application. Adsorption is a well known equilibrium separation process and an effective method for water decontamination applications [70]. Adsorption has been found to be superior to other techniques for water reuse in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances.

ADSORPTION

Adsorption techniques for wastewater treatment have become more popular in recent years owing to their efficiency in the removal of pollutants, which are difficulty treated with biological methods. Adsorption can produce high quality water while also being a process that is economically feasible. Decolorization is a result of two mechanisms (adsorption and ion exchange) and is influenced by many factors including dye/adsorbent interaction, adsorbent's surface area, particle size, temperature, pH and contact time.

Physical adsorption occurs when weak intraparticle bonds exist between the adsorbate and adsorbent. Examples of such bonds are van der Waals, hydrogen and dipole–dipole. In the majority of cases physical adsorption is easily reversible [71]. Chemical adsorption occurs when strong intraparticle bonds are present between the adsorbate and adsorbent due to an exchange of electrons. Examples of such bonds are covalent and ionic bonds. Two means that are useful to be developed are "chemisorption" and "physisorption". Chemisorption is a kind of adsorption which involves a chemical reaction between the surface and the absorbate. New chemical bonds are generated at the adsorbent surface. Examples include macroscopic phenomena that can be very obvious, like corrosion, and subtler effects associated with heterogeneous catalysis. The strong interaction between the adsorbate and the substrate surface creates new types of electronic bonds. In contrast with chemisorption is physisorption, which leaves the chemical species of the adsorbate and surface intact. It is conventionally accepted that the energetic threshold separating the binding energy of "physisorption" from that of "chemisorptions" is about 0.5 eV per adsorbed species. Chemisorption is deemed to be irreversible in the majority of cases [71].

Separation occurs because either the differences in molecular mass/shape or polarity causes some molecules to be held more strongly on the surface than others or the pores are too small to admit large molecules. However, amongst all the adsorbent materials proposed, activated carbon is the most popular for the removal of pollutants from wastewater [72, 73]. In particular, the effectiveness of adsorption on commercial activated carbon for removal of a wide variety of dyes from wastewaters has made it an ideal alternative to other expensive treatment options [73]. Because of their great capacity to adsorb dyes, activated carbon is the most effective adsorbent. This capacity is mainly due to their structural characteristics and their porous texture which gives them a large surface area, and their chemical nature which can be easily modified by chemical treatment in order to increase their properties. However, activated carbon presents several disadvantages [27]. It is quite expensive, the higher the quality, the greater the cost, non–selective and ineffective against disperse and vat dyes. The regeneration of saturated carbon is also expensive, not straightforward, and results in loss of the adsorbent. The use of carbons based on relatively expensive starting materials is also unjustified for most pollution control applications [74]. This has led many workers to search for more economic adsorbents as low–cost materials agricultural raw materials or even agricultural wastes. Furthermore, it is a great of importance a trend to polymeric dye adsorbents as chitosan.

CHITOSAN

There is abundant literature concerning the evaluation of adsorption performances of raw chitosan, especially in terms of adsorption capacity (amount of dye adsorbed) or uptake. In a batch system, the determination of the dye uptake rate by a chitosan–based material is often based on the equilibrium state of the adsorption system. At least 100 dyes, mainly anionic dyes, have been so far studied. Chitosan has an extremely high affinity for many classes of dyes. In particular, it has demonstrated outstanding removal capacities for anionic dyes such as acid, reactive and direct dyes. This is due to its unique polycationic structure. A proposed mechanism is to separate the textile effluents of dyeing reactor without any treatment and apply adsorption with adsorbents (i.e. chitosan) (Figure 1).

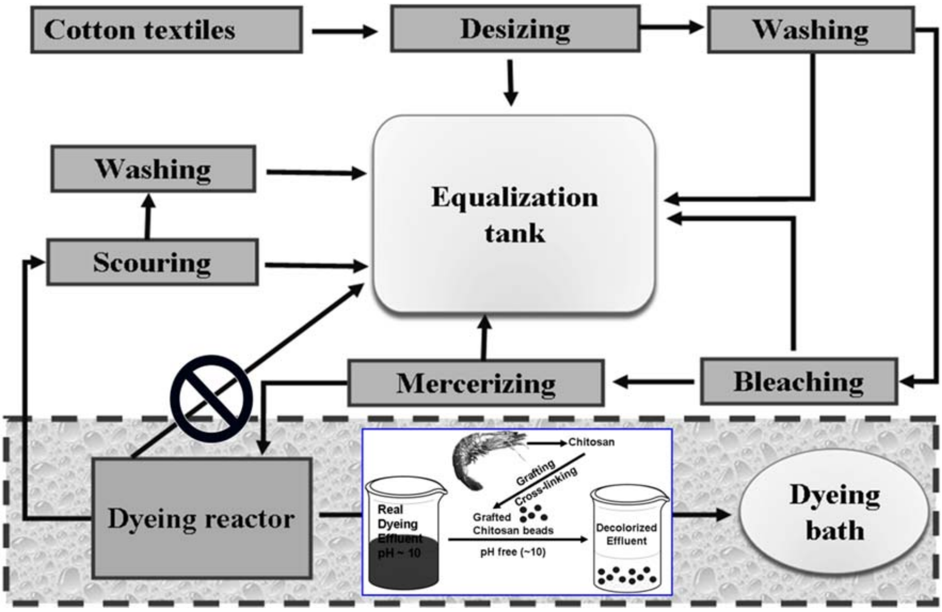

Figure 1. Proposed textile effluents decolorization with last step of adsorption.

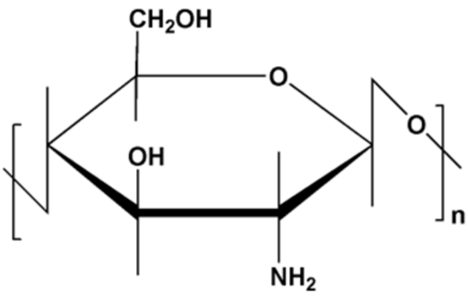

Figure 2.Chemical structures of chitosan.

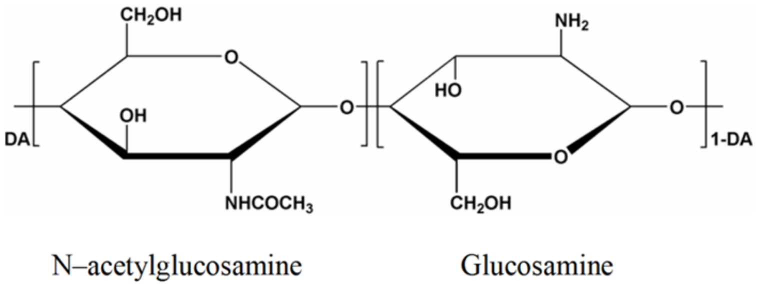

Figure 3. Chemical structures of commercial chitosan composed of N–acetyl glucosamine.

Furthermore, from a structural point of view, partial deacetylation of chitin results in the production of chitosan (Figure 2), which is a polysaccharide composed by polymers of glucosamine and N–acetyl glucosamine (Figure 3).

The effectiveness of chitosan for its ability to interact with dyes has been studied by numerous workers. Juang and co–workers [75–77] demonstrated the usefulness of chitosan for the removal of reactive dyes. They found that the maximum adsorption capacities of chitosan for RR 222, RB 222 and RY 145 were 1653, 1009 and 885 mg/g, respectively [76]. Annadurai [78–80] and Crini et al. [81] also reported that chitosan may be a useful adsorbent for the effluent of textile mills because of its high adsorption capacity. Uzun and Guzel [82–85] noted that chitosan can be used in the studies of dyestuff adsorption in comparison with most other adsorbents. This polysaccharide showed a higher capacity for adsorption of dyes than CAC and other low–cost adsorbents, as reviewed by Crini[86]. Kim and Cho [87] also indicated that the amount of RB 5 adsorbed on chitosan beads is much greater than on CAC. Similar conclusions were reached by Lima et al. [88] for the BB 9 adsorption. McKay's group [89–91] recently published a series of papers on the ability of chitosan to act as an effective adsorbent for the removal of acid dyestuffs from aqueous solution. The monolayer adsorption (saturation) capacities were determined to be 973.3, 922.9, 728.2 and 693.2 mg of dye per gram of chitosan for AO 12, AO 10, AR 73 and AR 18, respectively [89]. The interaction between chitosan and anionic dyes has also been intensively investigated by Guibal and co–workers [92–95]. Their investigations clearly indicated that chitosan had a natural selectivity for dye molecules and was very useful for the treatment of wastewater. They reported that adsorption capacities ranged between 200 and 2000 mmol/g for chitosan and between 50 and 900 mmol/g for CAC [94]. They concluded that chitosan exhibited a twofold or more increase in the adsorption capacity compared to CAC in the case of acid, direct, reactive and mordant dyes. The best choice for the adsorbent between CAC and chitosan depends on the dye, however, it was impossible to determine a correlation between the chemical structure of the dye and its affinity for either carbon or chitosan.

However, a strong advantage of chitosan is its modification ability. The basic idea of modifications is to make various changes in chitosan structure to enhance its properties (capacity, resistance etc). In particular, several researchers have proposed certain modifications in chitosan backbone to improve its adsorption capacity. These modifications are realized with grafting reactions [81, 96]. The modifications can improve chitosan's removal performance and selectivity for dyes, alter the physical and mechanical properties of the polymer, control its diffusion properties and decrease the sensitivity of adsorption to environmental conditions. Many scientists suggested chemical grafting specific ligands [97, 98]. However the only class for which chitosan [99] has low affinity is basic (cationic) dyes. To overcome this problem, the use of N–benzyl mono– and disulfonate derivatives of chitosan is suggested to enhance its cationic dye hydrophobic adsorbent properties and to improve its selectivity [81, 96]. These derivatives could be used as hydrophobic adsorbents in acidic media without any cross–linking reactions. To enhance and further develop the high potentials of chitosan, it is necessary to add/introduce chemical substituents at a specific position in a controlled manner [99]. This chemical derivatization promotes new adsorption properties in particular towards basic dyes in acidic medium or reactive/acid dyes in basic medium. Another study deals with the enzymatic grafting of carboxyl groups onto chitosan as a mean to confer the ability to adsorb basic dyes on beads [99]. The presence of new functional groups on the surface of beads results in increased surface polarity and density of adsorption sites and hence improved adsorption selectivity for the target dye. Other studies showed that the ability of chitosan to selectively adsorb dyes could be further improved by chemical derivatization. Novel chitosan–based materials with long aliphatic chains are developed by reacting chitosan with high fatty acids and glycidyl moieties [100]. In this way, these products could be used as effective adsorption materials for both anionic and cationic dyes. Other researchers suggested the use of cyclodextrin–grafted chitosan derivatives as new chitosan derivatives for the removal of dyes [101, 102]. These materials are characterized by a rate of adsorption and a global efficiency greater than that of the parent chitosan polymer [99].

The pure form of chitosan powders (raw) tends to present some disadvantages such as unsatisfactory mechanical properties and poor heat resistance. Another important limitation of the pure form is its solubility in acidic media and therefore it cannot be used as an insoluble adsorbent under these conditions (except after physical and chemical modification). The main technique to overcome these limitations is to transform the raw polymer into a form whose physical characteristics are more attractive. So, cross–linked beads have been developed and proposed. After cross–linking, these materials maintain their properties and original characteristics [103], particularly their high adsorption capacity, although this chemical modification results in a decrease in the density of free amine groups at the surface of the adsorbent in turn lowering polymer reactivity towards metal ions [92, 93]. The cross–linking agent is very important. Therefore many researchers studied the chitosan behaviour prepared with different cross–linkers, such as glutaraldehyde (GLA), tripolyphosphate sodium (TPP), epichlorydrine (EPI), ethylene glycol diglycidyl ether (EGDE), etc[3, 5, 104, 105]. The change in adsorption capacity was confirmed; the results showed that the chitosan–EPI beads presented a higher adsorption capacity than GLA and EGDE [5, 105]. They reported that these materials can be used for the removal of reactive, direct and acid dyes. It was found that 1 g chitosan adsorbed 2498, 2422, 2383 and 1954 mg of various reactive dyes (Reactive Blue 2, Reactive Red 2, Direct Red 81 and Acid Orange 12, respectively) [3]. As a comparison, it is specified that the adsorption capacities of commercially activated carbon for reactive dyes generally vary from 280 to 720 mg/g. Another advantage of EPI is that it does not eliminate the cationic amine function of the polymer, which is the major adsorption site to attract the anionic dyes during adsorption [105]. The cross–linking with GLA (formation of imine functions) or EDGE decreases the availability of amine functions for the complexation of dyes. With a high cross–linking ratio the uptake capacity decreases drastically. Among the conditions of the cross–linking reaction that have a great impact on dye adsorption are the chemical nature of the cross–linker, as mentioned above, but also the extent of the reaction. In general, the adsorption capacity depends on the extent of cross–linking and decreases with an increase in cross–linking density. When chitosan beads were cross–linked with GLA under heterogeneous conditions, it was found that the saturation adsorption capacity of reactive dyes on cross–linked chitosan decreased exponentially from 200 to 50 mg/g as the extent of cross–linking increased from 0 to 1.5 mol GLA/mol of amine. This is because of the restricted diffusion of molecules through the polymer network and reduced polymer chain flexibility. Also the loss of amino–binding sites by reaction with aldehyde is another major factor in this decrease. However, the cross–linking step was necessary to improve mechanical resistance, to enhance the resistance of material against acid, alkali and chemicals, and also to increase the adsorption abilities of chitosan. According to literature [3, 5, 104, 105], the adsorption capacity of non cross–linked beads was greater than that of cross–linked beads in the same experimental conditions. The materials, mainly cross–linked using GLA, have been also proposed as effective dye adsorbents by several researchers [101, 103]. The reaction of chitosan with GLA leads to the formation of imine groups, in turn leading to a decrease in the number of amine groups, resulting in a lowered adsorption capacity, especially for dyes adsorbed through ion–exchange mechanisms. Furthermore, it is noted that cross–linking can change the crystalline nature of chitosan, as suggested by the XRD diffractograms. After the cross–linking reaction, there was a small increase in the crytallinity of the chitosan beads and also increased accessibility to the small pores of the material.

It is evident from this brief literature survey that chitosan can be utilized as an interesting tool for the purification of dye–containing wastewater because of its outstanding adsorption capacity.

ACTIVATED CARBON

Activated carbon adsorption is one such method which has great potential for the removal of dyes from aqueous waste. The adsorption capacity of activated carbon depends on various factors, such as surface area, pore size distribution, and surface functional groups on the adsorbent, polarity, solubility, and molecular size of the adsorbate, solution pH and the presence of other ions in solution, and so on. The most widely used activated carbons are microporous and have high surface areas, and as a consequence, show high efficiency for the adsorption of low molecular weight compounds and for larger molecules. An adsorption study of methylene blue (MB) on activated carbon fiber (ACF) was also carried out. It has been used in adsorption systems including removal of noxious gases because of its extensive specific surface area, high adsorption capacity, well–developed micropores, reproducibility, and processability. The effects of various experimental parameters, such as the initial MB concentration and the ACF mass, on the adsorption rates were investigated. Equilibrium data was fit well by a Freundlich isotherm equation. Adsorption measurement shows that the process is very fast [106]. Nakagawa et al. [107] made attempt to evaluate the porous properties and hydrophobicity of activated carbons obtained from several solid wastes, namely, waste PET, waste tires, refuse derived fuel, and wastes generated during lactic acid fermentation from garbage. Activated carbons having various pore size distributions were obtained by the conventional steam–activation method and via the pretreatment method (i.e., mixture of raw materials with a metal salt, carbonization, and acid treatment prior to steam activation). The liquid–phase adsorption characteristics of organic compounds from aqueous solution on the activated carbons were determined to confirm the applicability of these carbons, where reactive dye (Reactive Black 5) was employed as representative adsorbate. Authors reported that the activated carbons with plentiful mesopores prepared from PET and waste tires had quite high adsorption capacity for large molecules. Therefore, they are useful for wastewater treatment, especially for removal of bulky adsorbates. Li et al. [108] reported the displacement of atrazine by the strongly competing fraction of natural organic matter (NOM) in batch and continuous–flow powdered activated carbon (PAC) adsorption system. The extent of atrazine displacement by NOM was found to be dependent on the type of PAC, while the rate of displacement was a function of PAC type as well as carbon dose. Choy et al. [109] reported the adsorption of three acidic dyes, Acid Blue 80 (AB80), Acid Red 114 (AR114), and Acid Yellow 117 (AY117) onto activated carbon. In the same paper, they have also reported the adsorption isotherms for the three single components (AB80, AR114, AY117) and three binary component (AB80+AR114, AB80+AY117, AR114+AY117), dyes adsorption on activated carbon. Four models for predicting the multi–component equilibrium sorption isotherms have been compared in order to determine the best to predict or correlate binary adsorption data. These four models are the extended Langmuir isotherm, the simplified model based on single–component equilibrium factors, a modified extended Langmuir isotherm with a constant interaction factor, and a modified extended Langmuir isotherm incorporating a surface coverage–dependent interaction factor. Adsorption of trichloroethylene (TCE) by two ACFs and two granular activated carbons pre–loaded with hydrophobic and transphilic fractions of NOM was examined by Karanfil et al. [110] ACF10. Also, the kinetics and mechanism of MB adsorption on commercially activated carbon and indigenously prepared activated carbons from bamboo dust, coconut shell, groundnut shell, rice husk, and straw have been reported by Kannan et al. [111]. Jirankova et al. [112] contribution deals with study of the combined adsorption–membrane process for organic dye removal. Adsorption equilibrium and kinetics of Egacid red sorption on PAC were studied in batch experiments. Tapered bed adsorption columns, using activated carbon, have been used to study the removal of two organic pollutants, an acid dye and parachlorophenol, from aqueous effluent by McKay et al. [113]. Equilibrium sorption isotherms were measured to provide the saturation capacity (Q_e) of each pollutant by ChemvironFiltrasorb 400 carbon, for operating continuous adsorption columns. The Redlich–Peterson (R–P) isotherm gives the best fit model to describe the sorption process of these organic pollutants. The conventional bed depth service time (BDST) model has not been applied to tapered beds before, as the linear velocity of fluid is continually changing along the column. Several others authors [114, 115] have also tested activated carbon for the adsorption of various dyes. Pereira et al. [66] reported that the surface chemistry of a commercially activated carbon has been selectively modified, without changing significantly its textural properties, by means of chemical treatments, using HNO_3, H_2O_2, NH_3, and thermal treatments under a flow of H_2 or N_2, and they found that the surface chemistry of the activated carbon plays a key role in dye adsorption performance. For cationic dyes (basic), the acid oxygen–containing surface groups show a positive effect but thermally treated samples still present good performances, showing the existence of two parallel adsorption mechanisms involving electrostatic and dispersive interactions. The conclusions obtained for each dye individually were confirmed in the color removal from a real textile process effluent.

Table 4. Previous studies of the adsorption of dyes using adsorbents based on agricultural solid wastes

Adsorbent	Dye	Ref
Sugar beet pulp	Gemazol turquoise blue–G	[125]
Powdered peanut hull	Sunset yellow, Amaranth, Fast green	[126]
Rice husk ash	Indigo Carmine	[127]
Chemically modified peanut hull	Methylene blue, Brilliant cresyl blue, Neutral red, Sunset yellow, Fast green	[128]
Peanut hull	Methylene blue, Brilliant cresyl blue, Neutral red	[129]
Coir pith activated carbon	Reactive orange 12, Reactive red 2, Reactive blue 4	[130]
Coir pith activated carbon	Congo red	[131]
Coir pith carbon	Methylene blue	[132]
$ZnCl_2$ activated coir pith carbon	Acid brilliant blue, Acid violet, Methylene blue, Rhodamine B	[133]
Coir pith	Acid violet	[120]
Rice husks activated carbon	Malachite green	[134]
Rice husk–based porous carbon	Malachite green	[135]
Rice husk	Congo red	[136]
Tea waste	Methylene blue	[137]
Coniferous pinus bark powder	Crystal violet	[138]
Orange peel activated carbon	Direct Blue–106	[139]
Neem sawdust	Malachite green	[140]
Guava seed carbon	Acid blue 80	[141]
Peanut hull	Reactive Black 5	[142]
Loofa activated carbon	Reactive orange	[143]
Apricot stone activated carbon	Astrazon yellow (7GL)	[144]
Almond shells	Direct red 80	[145]
Lemon peel	Malachite green	[146]
Bagasse fly ash	Methyl violet	[147]
*Polygonum*orientale Linn activated carbon	Malachite green	[148]

Another source of activated carbon is agricultural wastes. A very detailed review of Demirbas[116] and Sharma [117]. Plentiful agricultural waste and various unused plant parts offer an inexpensive and renewable additional source of activated carbon (AC). These waste materials have little or no economic value and often pose a great disposal problem. So these waste materials are used in treated and untreated form for the removal of dyes. A wide variety of activated carbon prepared from agro–waste such as pine wood, corn cob, fruit stones, nut shells, cassava peel, tapioca peel, bamboo, bagasse, rice husk, bark, leaves and used tea leaves are described by Sharma [117].

Application of activated carbon prepared from rice husk, was estimated as a potential adsorbent for the removal of Malachite green and found to be having good adsorption capacity comparative to the activated carbon prepared from banana peel [118], date pits [119], rice husk [111], wood saw dust [120], orange peel [118], sugarcane dust [121]. Garg et al. [122] demonstrated that adsorption efficiency of sulphuric acid treated saw dust was higher than formaldehyde treated saw dust for the removal of malachite green. It was concluded that ACR adsorption efficiency was unaffected by pH, while pH=6–9 was optimum for dye removal by SDC and SD. The adsorption of ash prepared from rice husk was found to be an effective adsorbent because of their high surface area and the volume. The maximum monolayer capacity estimated was 690 mg/g. Moreover the adsorption was maximum on the ash compared to the activated carbon prepared from the rice husk after calcinations because of the presence of both silica and carbon. The adsorption characteristics of Direct Red 23 (DR23) on to mangrove bark (Rhizopusapiculata) that has been previously treated with formaldehyde in acid medium was investigated and ob–served that dye sorption decreases at high pH values in accordance with the ion exchange mechanism of the adsorption and maximum removal was at 2. The monolayer sorption capacity of modified bark for Direct Red 3 (DR3) sorption was found to be 21.55 mg/g.

AGRICULTURAL WASTES

There have been many attempts to find inexpensive and easily available adsorbents to remove the pollutants such as the agricultural solid wastes where according to their physicochemical characteristics and low cost they may be good potential adsorbents [123]. Agricultural productions are available in large quantities around the world; thus big amount of wastes rejected. Table 4 shows agricultural production (ton/year) in some countries. Agricultural wastes are lignocellulosic materials that consist of three main structural components which are lignin, cellulose and hemicelluloses. These components contribute mass and have high molecular weights. Lignocellulosic materials also contain extractive structural components which have a smaller molecular size [116]. Agricultural wastes are renewable, available in large amounts and less expensive as compared to other materials used as adsorbents. Agricultural wastes are better than other adsorbents because the agricultural wastes are usually used without or with a minimum of processing (washing, drying, grinding) and thus reduce production costs by using a cheap raw material and eliminating energy costs associated with thermal treatment [124]. There are specific alternative agricultural by–products used intensely as dye adsorbents such as peanut hull, coir pith and rice husk as listed in Table 4, which shows previous studies of the adsorption of different dyes using adsorbents based on agricultural solid wastes.

BACTERIALS

A wide variety of fungal organisms are capable of decolorizing a wide range of dyes [64, 149]. Many genera of fungi have been employed either in living or inactivated form. The use of white–rot fungi such as Phanerochaetechrysosporium in decolorizing textile wastewater has been widely reported in literature [150–157]. There are various fungi other than white–rot fungi, such as Aspergillusniger [149, 158, 159], Rhizopusarrhizus [160], Rhizopusoryzae [161] which can also decolorize and/or biosorb diverse dyes. For living cells, the major mechanism is biodegradation because they can produce lignin modifying enzymes, laccase, manganese peroxidase (MnP) and lignin peroxidase (LiP) which due to their unspecific activity is the first step in the process of mineralization of dyes [162]. The relative contributions of LiP, MnP and laccase to the decolorization of dyes may be different for each fungus. In addition to biodegradation, a biosorption mechanism might also play an important role in the decolorization of dyes by living fungi. For dead cells, the mechanism is biosorption, which involves physicochemical interactions such as adsorption, deposition, and ion exchange. Decolorization of dye wastewater by fungal biomass has been extensively reviewed by Fu and Viraraghavan [64], Kaushik and Malik [163], and Singh [164]. Limited information is available on interactions betweendead fungal biomass and a variety of dyes with complex molecular structures. Fu and Viraraghavan[165] studied the roles played by functional groups such as carboxyl, amino, phosphate and lipid fractions present in fungal biomass from A. niger in biosorption of four different dyes. In biosorption of Basic Blue 9 on A. niger, carboxyl and amino groups were found to be the main binding sites while in biosorption of Acid Blue 29, only amino group was a major site and electrostatic attraction was believed to be the primary mechanism. In biosorption of Congo Red, the amino, carboxylic acid, phosphate groups and lipid fractions were all found to be important binding sites and in addition to electrostatic attraction, other mechanisms were also believed to be involved in biosorption. In biosorption of Disperse Red 1, physical and chemical adsorption along with electrostatic attraction was found to be the mechanism of biosorption while amino group and lipid fractions were the major binding sites.

CONCLUSION

Adsorption is characterized as the most promising decolorization technique. Various types of adsorbents were studied in order to remove the dyes from textiles effluents. The main dye adsorbents reported are activated carbon and chitosan. The main advantage of activated carbon is its high adsorption capacity, but it presents high regeneration cost. On the contrast, chitosan after various modifications can increase its adsorption capacity. Its reuse potential is attributed to the easy dye desorption from chitosan with pH–adjusted conditions. Recently, other materials, more economical, have been attempted to be used as adsorbents at the tertiary stage of effluent's treatment replacing chitosan and activated carbon: natural materials, biosorbents, waste materials from industry and agriculture), clay materials (bentonite, kaolinite), zeolites, siliceous material (silica beads, alunite, perlite), agricultural wastes (bagasse pith, maize cob, rice husk, coconut shell), industrial waste products (waste carbon slurries, metal hydroxide sludge, coffee wastes), biosorbents (chitosan, peat, biomass) and others (starch, cyclodextrin, cotton). The turn of research to low–cost materials from mainly agricultural raw sources or agro–based wastes is nowadays dominated.

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