

# Natural biocomposites for removal of hazardous coloring matter from wastewater: A review

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## Abstract

Naturally producing or artificially manufactured biocomposite materials are highly valuable for removing colored substances or hazardous compounds from wastewater. They are relatively efficient to clean up the environmental pollutants due to their unique adsorption potentials, nutrient recycling, chelating ability and anti-bacterial effects. These characteristics have found significant applications in removal of heavy metals and dyes from wastewater through existing techniques of biosorption and coagulation. This review article provides detailed information after extensive literature review about colorants, their classification, sources, applications and toxicity, various treatment methods and characteristic dye adsorption properties. One of the objectives of this review article is to organize the scattered available information about the potentially effective biocomposites adsorbents, their properties and characteristic adsorption capacities for removing dyes. This study presumes that the biodegradable polymer materials are one of the rising regions in removing toxic colored species from textile waters. The effectiveness of various adsorbents has been presented together with various treatment processes such as chemical, physical and biological methods are utilized to control physicochemical parameters, like chemical oxygen demand, biological oxygen demand, total organic carbon and dissolved organic matter. This review showed that chitosan/hydrogel/SiO<sub>2</sub> prepared by sol-gel method showed minimum adsorption capacity 0.080±0.005 and β-cyclodextrin-chitosan modified Fe<sub>3</sub>O<sub>4</sub> nanoparticles showed highest adsorption capacity of 2780 mgg<sup>-1</sup> for removing methyl blue dye. The study concluded that biopolymer-based composites and blends can suitably address the challenge raised by their synthetic counterparts.

**Keywords:** Wastewater Treatment, Dyes, Advanced Oxidation Techniques, Biocomposite Materials, Chitosan Composites, Polyaniiline Composites

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## 1. Botany

### 1.1 Introduction

Textile industries consume huge volumes of water as well as chemicals of diverse composition ranging from polymers and organic products to inorganic compounds. Due to massive discharge of colored substances in high concentrations, dyeing industry is one of major contributors of environmental pollution. The appearance of colorants in effluents even at very low concentrations is highly undesirable and visible. It is not only harmful to human bodies and ecologies but also to biological species. About 140,000 new chemicals have been made since 1950 and these chemicals have turned out to be broadly dissipated in earth's atmosphere [1].

Wastewater from textile units discharges various natural or synthetic compounds, a substantial number of which are non-biodegradable and harmful. In order to fortify the safety and quality of water structures, it is incredibly significant to perceive the attributes of textile wastewater Sajid et al., 2018

and screen their contribution in aquatic ecosystem. In 1974, Ecological and Toxicological Association of Dyestuffs Manufacturing Industry (ETAD) came into existence in order to minimize the damage to environment and fully cooperate with government sector to overcome the concerns of public over the toxicological impacts of articles manufactured by companies [2-3].

Sanitation of cities and towns and consequently, safe disposal of wastewater is the first and utmost purpose when treating wastewater. Today, wastewater reuse is relatively new concern and serves as another purpose of wastewater treatment. During 20<sup>th</sup> century, technological based practice of reclaimed water started at huge scale due to exponential increase in pollution as a result of rapid rise in population. Today, wastewater treatment units are installed in every big city, and tons of treated wastewater is available for reuse [4].

## 2. Colorants

Substances with the ability of transmitting their shade to medium or substrate are referred as colorants. They are used either alone or in combination with different chemicals which produce or change color of desired product. Colorants are widely used in paints, textiles, ceramics, prints, plastics and photographic industries. They are widely used in food appetizers to create impressions and to make products attractive [5-6]. They are classified into two categories: pigments and dyes.

## 2.1 Classification of Colorants

Colorants are categorized into dyes and pigments. These can be further classified as follows (Fig.1).

### 2.1.1 Pigments

According to Color Pigments Manufacturers Association Inc. (CPMA), pigments are defined as particulate organic or inorganic substances which usually exhibit white, black or colored solids usually insoluble and unaffected by physical or chemical medium or substrate in which they are introduced. Dyes and pigments originate from same building blocks but differ in solubility as dyes are soluble in the incorporated media whereas pigments are insoluble and require physical mixing with medium. Generally, they constitute inorganic as well as organic insoluble substances. Due to their high coloring power and durability organic dyes (insoluble) can be used to replace pigments. Pigments are considered as powdered compounds mixed with liquid used for surface coatings. Due to the phenomenon of scattering of light and selective absorption, they alter their appearance. They are used for manufacturing paints, polymeric substances and inks and usually dispersed in the medium for application use. They are mostly found in toothpaste, decorative skin care products and eye shadows. Pigments are mostly found in particulate form as well as powdered forms in metals and alloys. Pigments are prone to light, highly sensitive to pH change, temperature and heat and oxygen integration [7].

#### 2.1.1.1 Classification of Pigments

##### (A) Organic Pigments

These pigments contain carbon rings or carbon chains as well as metallic parts for stabilization of organic parts. Their performance depends on various parameters such as surface properties, their crystallinity and chemical structure, particle size as well as size distribution. They are used to enhance tinting strength and shades [4-8]. Their classification on the basis of chemical structure is given in detail below [9]:

##### (B) Inorganic Pigments

These pigments are not based on carbon and consist of solutions based on metallic salt precipitation. Chemical, mechanical and heat treatments are performed on the raw pigment materials even if the pigments are present in precipitated form. Due to their optimum particle size, they are rendered as opaque substances. They are highly resistant towards higher heat stability, pigment bleeding and

migration, light fastness, and stable towards organic solvents. Examples of inorganic pigments include lead chromate, iron oxide, chromium oxide green, iron blue, chrome green, bivanadate, manganese oxide, mixed metal oxide and phthalochrome green [9].

## 2.2 Dyes

In ancient times, natural dyes were obtained from plant sources but mechanisms of staining colors and chemical information were unavailable [5-6]. Dyes are defined as intensely fluorescent or colored organic compounds which give color to substrate by the process of selective absorption of light. They are water soluble and go through an application process which sometimes distorts crystal structure by absorption, ionic or covalent bonds or by solution and mechanical retention. They are both positively and negatively charged and anion contributes to the color portion of molecule. Dyes are taken as the organic mixtures with attractive colors because of chromophore and conjugated system, presence of auxochromes, resonance of electrons and absorption of light from UV spectrum [5-6]. They are water soluble and possess special affinity towards substrate and bind itself towards substrate. Dyes are classified in terms of structure, color and application.

### 2.2.1 Classification of Dyes

Dyes are classified on the basis of structure, sources and applications.

#### 2.2.1.1 Classification Based on Sources

On the basis of sources, dyes are further divided into natural and synthetic dyes described below:

##### 2.2.1.1.1 Synthetic Dyes

These are derived from inorganic and organic compounds and primarily made from chrome and aniline. Synthetic dyes are used in large scales in dyeing and printing industries. They vanish easily and fade away when exposed to sunlight. Aniline dyes are sometimes, called coal tar dyes according to degree of brightness or light fastness. Chrome dyes are non-corrosive and color fast. While dealing with synthetic dyes parameters such as machine washability, fading, dry cleaning, perspiration, steam pressing, boiling, hot pressing, gas fume fading and salt water are taken into consideration. These dyes causes severe effects on human body when exposed to large dosages [4-8].

##### (A) Water Soluble Dyes

Direct dyes are anionic water soluble dyes having substantial affinity for cellulosic fibers. Poly azo substances as well as oxazines, stilbenes, phthalocyanines constitute major portion of direct dyes. They are principally used for dyeing regenerated cellulose, cotton, leather, paper and nylon to a lesser extent. Acid dyes find their application in wool, nylon, silk and modified acrylics. These anionic dyes are water soluble and to some extent used in food, cosmetics, paper, inkjet and leather industries. Basic dyes are chemically classified into cyanine, thiazine, oxazines, acridine, triarylmethane and diazahemicyanine. Earlier,

cationic dyes were used for silk, wool and tannin mordanted cotton for brighter shades. They are applied to paper, modified nylons, polyacrylonitrile and modified polyesters. Cationic dyes exhibit biological activities and therefore, used in field of medicine as antiseptics. Basic dyes produce colored cations in solution [10].

### (B) Water Insoluble Dyes

Antraquinone and andigoid are principal chemical classes of vat dyes. They are applied to cellulosic fibers in the form of soluble leuco salts after reduction with sodium hydrogen sulfide in an alkaline bath. Leuco forms are further re-oxidized into keto forms (insoluble) during exhaustion onto fiber. To redevelop crystal structure soaping is performed in after treatment procedures. Sodium sulfide as reducing agent in an alkaline bath is used for application of sulphur dyes on cotton [4]. They are an important class from economic viewpoint due to their cost effectiveness. They possess excellent wash fastness properties and numerically a small group of dyes [10]. Solvent dyes are water insoluble but soluble in other solvent mediums. They lack poplar solubilizing group such as carboxylic acid, quaternary ammonium and sulfonic acid. Azo, anthraquinone and to a lesser extent triaryl methane and phthalocyanine are categorized under solvent dyes [10].

#### 2.2.1.1.2 Natural Dyes

Dyes with natural sources as their origin are called natural dyes. They are obtained from minerals invertebrate animals and plants commonly from vegetable sources such as roots, leaves, wood, bark, berries and leaves as well. Archeological sources of these dyes include lichens and fungi. These colorants produce earthly shades but give beautiful shades when merged with mordants [11-12]. Some commonly used mordants include iron for enhancing and color darkening, alum with cream of tartar to promote brightness and evenness, tin with cream of tartar for enhancing and brightening color. Tannic acid is used for brown and tans and blue vitriol is used to bring out green shade and it is used to sadden color [9]. Natural dyes do not strain adjacent fibers during washing process due to their non-substantivizes nature. Advantages of these dyes include cost effectiveness and less disposal problems due to their biodegradability. Preparation of these dyes involve mild type of reactions and they completely harmonize with nature [9]. There are two possible types of natural dyes as explained below.

#### (A) From Plants

Dark mustard yellow obtained from Gamboge tree resin and brown color from Cudbear catechu and red shade from pomace plant are some of the colors obtained from plants [13-15]. The specified shades with names of respective specie are provided in the table below:

Table 2 Plant species and their respective shades [9]

Sr. No.	Plant Species	Shades Obtained
1	Brazil Wood	Bright red shade

2	Log Wood	Black and blue in silk, Purple on wool
3	Fustic Young or Zante	Yellow to dark Olive shade
4	Fustic Old	Gold to yellow shade
5	Madder and Kermes	Red
6	Quercitron	Brown to yellow shade
7	Lac	Bright red color
8	Indigo	Blue color
9	Cutch	Rich brown shade
10	Annatto	Fugitive red and orange
11	Cudbear	Lilac color

#### (B) From Animals

Animals are also used to obtain color. Several examples include murex snail to obtain purple color, lac insect produces red and violet colors, octopus/cuttlefish gives sepia brown color. Cochineal insects produced from cactus plants give brown color. Female insects are dried in sun and their bodies are further ground to obtain rich red powder, when solubilized in water gives vibrant red color. This technique was discovered by pre-Colombian Indians.

#### 2.2.2 Applications of Dyes

The applications of different dyes are shown in figure 2 as shown below.

#### 2.2.3 Toxicity of Dyes

Synthetic dyes are toxic water pollutants due to their solubility properties and these are very often found in industrial wastewaters in trace quantities. The magnitude of the problem can be indicated by the fact that two percent of dyes that are produced are released directly in water reserves [17]. Since the dyes are resistant to aerobic digestion, recalcitrant organic molecules that are stable to light, oxidizing agents and heat, therefore, it is hard to treat wastewater containing dyes [18]. Several chemical, physical and biological decolorization methods have been detailed and used during past three decades however few methods have been accepted by the textile and paper industries. Several reported methods for the removal of toxic chemicals from effluents are detailed below.

#### 2.2.4 Factors Affecting Adsorption of Dyes

Initial concentration of dye, contact time, pH and temperature are some of important parameters affecting dye adsorption. Thus, effects of these factors are considered and optimized to obtain efficient results. These factors and their influence are discussed below:

#### (A) Effect of Amount of Adsorbent

By increasing adsorbent dosage percentage, dye removal increases due to an increase in sorption sites on the surface of adsorbent. It is a major parameter to determine the capacity of adsorbent at given amount of adsorbent dosage. It is considered as an important factor from economic point of view, as the adsorbent dosage gives an idea about smallest amount of adsorbent required for dye

adsorption. Table shows the studies reported on percentage dye removal and effect of adsorbent dosage.

### **(B) Effect of pH**

Efficiency of adsorption process depends on pH of medium, since any change in pH affects the surface properties of adsorbent as well as degree of ionization of adsorptive substance [32]. The electro-kinetic properties are quantified by PZC (point of zero charge). It is defined as pH at which surface charge is zero and is commonly used for systems in which potential determining ions are  $H^+/OH^-$ . Due to presence of functional groups such as  $H^+$  ions, anionic dye adsorption is favored at  $pH < pH_{pzc}$  when the surface of adsorbent becomes positively charged. Anionic dye adsorption is favorable at  $pH > pH_{pzc}$  when functional groups such as  $OH^-$  are favored [33].

### **(C) Effect of Initial Dye Concentration**

The effect of initial dye concentration is dependent upon the relationship between the available sites on surface of adsorbent and concentration of dye. Generally, percentage dye removal is reduced by increasing initial dye concentration. Therefore, amount of dye removal highly depends upon initial dye concentration. Increase in initial dye concentration increases the capacity of adsorbent and this may be due to high driving force for mass transfer at high initial dye concentration [43].

### **(D) Effect of Temperature**

Another significant physiochemical factor that affects adsorption capacity of adsorbent is temperature. Adsorption is endothermic process, where increase in temperature notably enhances the process of adsorption. This can be explained by the reason that by increasing temperature the mobility of charged substances and molecules present in dye increases that leads to an increase in number of active sites thereby increasing adsorption. If increasing temperature decreases the adsorption capacity then adsorption is exothermic process. This effect is explained by the decrease in adsorptive forces between active sites of adsorbent and molecules of dye, thereby, decreasing adsorption of dye [52].

## **3. Treatment Methods**

Depending on the nature and type of the effluents, treatment process can be based on the conventional technologies including physical, biological and chemical methods.

### **3.1 Physical Treatment**

Sedimentation is one of the primary treatments to remove suspended solids after the removal of oil, grease, solid particles and gritty materials. This process is performed to reduce the carrying capacity of secondary treatment and effectively remove different sediment particles from the waste containing higher concentration of settleable solids. Sedimentation tanks having horizontal flow are used with center feed circular clarifiers and gravity separation method is utilized for separation of waste.

Reverse osmosis is also considered as hyper filtration: water passes powerfully through partially permeable membranes. Osmotic pressures for the procedure determines the amount of dissolved salt [60]. Nanofiltration can be successfully utilized for dye removal [61]. Nanofiltration involves handling of solutions with complex and high concentrated solutions. Almost 85-90% of dye maintenance speed is acceptable for recycling of water [62].

### **3.2 Chemical Treatment**

Ozonation procedure involves effective decolorization of wastewater depending on their chemical composition. The chemical structure of dye under treatment is responsible for the speed of photo-degradation. The process is advantageous as it neither increases the amount of sludge nor the quantity of wastewater [63]. Fenton process involves mechanism of an electron transfer between a homogeneous metal catalyst ( $Fe^{+2}$ ) and hydrogen peroxide ( $H_2O_2$ ). During Fenton reaction, hydrogen peroxide is catalyzed by ferrous ion to give hydroxyl radicals as a product [64].

### **3.3 Biological Treatment**

Various aerobic methods are being used extensively in the dairy field. These methods include activated sludge processes and aerated lagoons [65], a batch reactor involving membrane sequencing [66], rotating biological contactors [67] and trickling filters [68]. Water containing all the organic matter with exceptions like ether and hydrocarbons, can be removed by aerobic treatment of water. The activated sludge system is established and extensively studied and recent results indicated that full-scale activated sludge systems present a core microbiome whose activity is responsible for wastewater decontamination [69-70]. It involves biogenic enzymatic wastewater treatment. For removal of wastes loaded with organic pollutants, bioremediation is the most effective tool. Microorganism plays an important role in mineralization of recalcitrant nature of molecules and multifaceted organic molecules [71]. Almost 70% of organic materials are degraded by biological treatment [72].

## **4. Analysis Methods**

Conventional physical and chemical parameters, such as total organic carbon (TOC), chemical oxygen demand (COD) and biological oxygen demand (BOD) cannot provide enough information to differentiate pollution from various sources. Dissolved organic matter is a heterogeneous mixture of organic polymers that can easily pass through a nominal pore size filter usually between  $0.1 \mu m$  and  $1.0 \mu m$  [73]. It is ubiquitous in wastewaters as well as in all natural water bodies [74]. By characterizing various types of wastewater can facilitates the identification in receiving water sources [75]. Various methods have been developed for dye analysis, some instrumental methods of analysis include spectroscopic methods i.e. spectrophotometry [76-77], Raman spectrometry [78],

infrared spectrometry [79], mass spectrometry (MS) methods [80] various chromatographic methods such as high performance liquid chromatography (HPLC) and thin layer chromatography [81] and capillary electrophoresis [82]. Spectroscopic methods are preferred because they are non-destructive, but their discriminating power for mixed dyes is not good enough [83].

**4.1 Biocomposite Materials**

Composites are defined as mixture of two or more ingredients where one is called as reinforcement required in smaller quantity and other is called matrix which is required in larger quantity. Biocomposite materials have acquired greater attention from scientific society for removal of colored entities from wastewater by applying various processes. The aspiration of the investigation is to examine effectiveness of biocomposites for removing pollutants from wastewater. These materials are non-mutagenic, non-toxic and non-carcinogenic, bioactive compounds blended with alginate, chitosan, lignin, chitin, starch, cellulose and hemicellulose. These composite materials are formed by natural polymers and resin i.e. matrix. In past few years, these serious concerns due to global warming and pollution have forced researchers to develop composites based on environmentally sustainable, environment friendly and biodegradable polymers [84].

**4.2 Chitosan Composites**

Chitosan consist of an unbranched binary hetero-poly-saccharide having two randomly distributed units  $\beta$ -(1-4)-linked D-glucosamine i.e. deacetylated unit and N-acetyl-D-glucosamine i.e. acetylate unit. Its structure is similar to that of cellulose which is obtained by partial deacetylation of the natural product chitin. Chitosan is prepared by the alkaline deacetylation of chitin (second most abundant polysaccharide in nature after cellulose). Chitosan forms an intra and inter molecular hydrogen bonding due to the hydroxyl and amine groups, therefore, chitosan forms a rigid crystalline structure [85]. Chitosan is insoluble at natural and alkaline pH values because of the pKa value of chitosan of about 6.5 but soluble in an acid solutions [86].

**4.3 Polyaniline Composites**

Polymers have acquired considerable attention in recent era due to their wide range of applications, metal conductivity and potential use in nano-devices. Polyaniline is a conducting polymer and polymerization can be used to achieve required composites. Wastewater treatment can also be performed using polyaniline composites. Some examples are mentioned below:

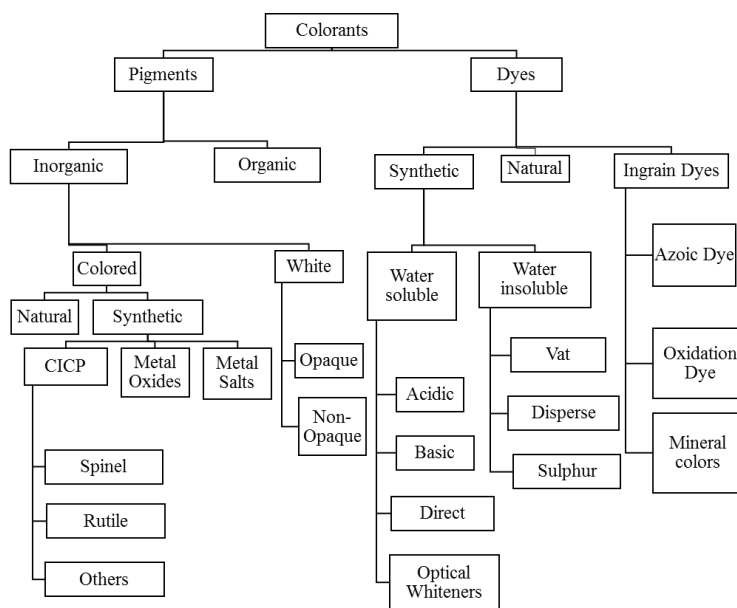


Fig 1 Schematic representation of colorants

Table 1 Classification of pigments

Sr. No.	Types of Pigments	Family
1	Violet	Quinacridone and Dioxazine
2	Blue	Anthraquinone and Phthalocyanine
3	Green	Phthalocyanine
4	Yellow	Mono-azo-salt, Diazo-Pigment, Isoindolinone and Anthraquinone
5	Brown	Diazo Pigment
6	Red	Naphthol Lake, BONA Lake, Quinacridone, Diazo Pigment, Anthraquinone, DPP and Diketopyrrole Pyrrole
7	Azo	Azo Lakes, Naphthol, Diazo, Diazo Condensation, Naphthol AS, Metal Complex,

		Benzimidazolone, Mono Azo Yellow and Orange
8	Polycyclic	Anthraquinone, Phthalocyanine, Quinacridone, Thioindigo, Dioxazine, Perylene and Perinone, Triarylcricarbonium, Quinophthalone, Isoindolinone, Isoindoline and Diketopyrrole-Pyrrole-Pyrrole

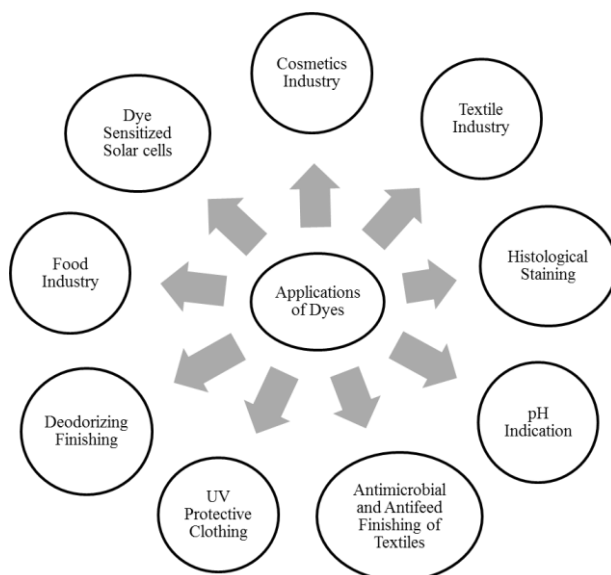


Fig 2 Application of dyes [16]

Table 3 Effect of adsorbent dosage

Adsorbents	Amount of Adsorbent	Dyes	Percentage Removal	References
Treated sawdust	0.2-1 g/100mL	Malachite Green	18.6-86.9%	[19]
Rice hull	0.02-0.08 g	Reactive Orange 16	21.7-56.2 %	[20]
Orange peel	50-600 mg/50 mL	Acid Violet 17	15-98 %	[21]
Treated sawdust	1-30 gL <sup>-1</sup>	Brilliant Green	61-99.9 %	[22]
Cashew nutshell	5-30 gL <sup>-1</sup>	Congo red	56.3-99.3 %	[23]
Tea waste	2-20 gL <sup>-1</sup>	Acid Orange 7	90-99 %	[24]
Tea waste	2-20 gL <sup>-1</sup>	Basic yellow 2	19-60 %	[24]
Modified mango seed	0.1-1.2 g	Methylene Blue	99.8-79 %	[25]
Raw mango seed	0.1-1.2 g	Methylene Blue	99.5-68 %	[25]
Modified sawdust	1.5-5 g	Methylene Blue	34.4-96.6 %	[26]
Fly ash	8-20 g	Methylene Blue	45.16-96 %	[27]
Kaolin	0.25-4 gL <sup>-1</sup>	Crystal Violet	75-97 %	[28]
Modified Alumina	5-20 gL <sup>-1</sup>	Crystal Violet	58-99 %	[29]
Pine cone	0.01-0.03 mg	Congo red	13.45-18.96 %	[30]
Chitosan/Alumina	1-12 gL <sup>-1</sup>	Methyl Orange	92.48-99.23 %	[31]

Table 4 The pH range and adsorbents

Adsorbents	pH Range	Dyes	Percentage Removal	References
Modified Alumina	2.6-10.8	Crystal violet	20-80%	[29]
Activated Clay	2-9	Methylene blue	60-95%	[34]
Kaolin	2-7	Crystal violet	65-95%	[35]
Bentonite	1.5-11	Acid blue 193	Decrease in %	[36]
Activated Carbon	2-11	Methylene blue	Increase in %	[37]
Fly Ash	2-8	Methylene blue	36-45%	[27]
Modified Saw Dust	2-11	Methylene blue	Increase in %	[26]
Tobacco Stem Ash	2.08-7.93	Methylene blue	60-81%	[38]
Pine Cone	3.47-7.28	Methylene blue	63.83-94.82%	[39]
Pine Cone	3.55-10.95	Congo red	60.5-5.75%	[39]
Pine Leaves	2-11	Methylene blue	20-80%	[40]
Fe <sub>2</sub> O <sub>3</sub>	1.5-10.5	Acid red 27	98-27%	[41]

Activated Rice Husk	2-9	Acid Yellow 36	80-45%	[42]
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Table 5 Effect of initial dye concentration on dye adsorption by various adsorbents

Adsorbents	Initial dye concentration	% age removal	Dyes	References
Bentonite	100-250 mg/L	Decreases in %	Acid Blue 193	[44]
Red Mud	10-40 mg/L	26.2-12.52 %	Acid Violet	[45]
Fly Ash	5-30 mg/L	99-84 %	Congo Red	[46]
Kaolin	10-40 mg/L	90-62 %	Methylene Blue	[47]
Apricot Seed	50-500 mg/L	91-62 %	Astrazone Black	[48]
Modified Mango Seed	50-250 mg/L	99.1-96.9 %	Methylene Blue	[25]
Raw Mango Seed	50-250 mg/L	99.1-92.5 %	Methylene Blue	[25]
Rice Husk	10-30 mg/L	82.5-71 %	Malachite Green	[49]
Sugarcane Bagasse	100-500 mg/L	99.1-87.1 %	Rhodamine B	[50]
Sugarcane Bagasse	250-500 mg/L	94-55.5 %	Basic Blue 9	[50]
Activated Carbon	30-150 mg/L	45-10 %	Eriochrome black T	[51]
Modified Sawdust	25-500 mg/L	91.2-66.3 %	Methylene Blue	[26]
Pine Leaves	10-90 mg/L	96-41 %	Methylene Blue	[40]

Table 6 Effect of temperature on various adsorbents

Adsorbents	Type of Process	Dyes	Temperature	References
Peanut Husk	Exothermic	Indosol Black	303-333 K	[53]
Residue Sludge	Endothermic	Naphthol Green B	288-323 K	[54]
Residue Sludge	Endothermic	Congo Red	288-323 K	[54]
Treated Rice Husk	Endothermic	Methylene Blue	293-313 K	[55]
Sugarcane Bagasse	Endothermic	Basic Blue 9	303-323 K	[50]
Sugarcane Bagasse	Endothermic	Rhodamine B	303-323 K	[50]
Kaolin	Exothermic	Congo Red	298-333 K	[56]
Sodium Bentonite	Exothermic	Congo Red	298-333 K	[56]
Modified Ball Clay	Endothermic	Methylene Blue	303-313 K	[57]
Raw Ball Clay	Endothermic	Methylene Blue	303-313 K	[57]
Pine Leaves	Endothermic	Methylene Blue	303-333 K	[40]
Activated Clay	Endothermic	Methyl Orange	293-303 K	[58]
Saw Dust	Endothermic	Tartrazine	298-318 K	[59]

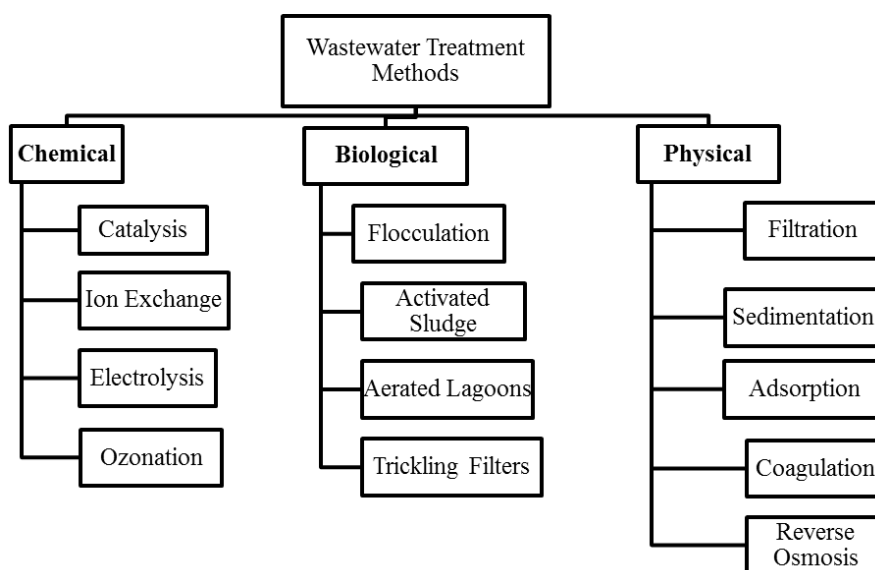


Fig 3 Schematic representation of wastewater treatment methods

Table 7 Advantages and disadvantages of dye removal methods [52]

Physical/Chemical Methods	Advantages	Disadvantages
<b>Physical Treatments</b>		
Membrane Filtration	Removal of all types of dye	Concentrated sludge production

Electro-kinetic Coagulation	Economically feasible	Production of sludge
Wood Chips	Adsorption capacity for acidic dyes is fine	Retention time is longer
Peat	Cellular structure makes it good adsorbent	Surface area specified for adsorption of dyes are lower than activated carbon
Adsorption by Activated Carbon	Can be used for range of dyes	High cost
Silica Gel	Efficient for removing basic dyes	Side reactions block commercial applications
Ion Exchange	Regeneration of adsorbent: no loss	Not effective for all dyes
Irradiation	Effective oxidation at lab scale	Dissolved oxygen is required in large amount
Cucurbituril	Good sorption capacity for range of dyes	Expensive
<b>Chemical Treatments</b>		
NaOCl	It starts and promotes azo bond cleavage	Release of aromatic amine
Electrochemical Destruction	Compounds broken down are non-hazardous	Electricity expense
Photochemical	No sludge production	Byproducts formation
Ozonation	Gaseous state application: no alteration of volume	Short half-life of 20 minutes only
Fenton's Reagent	Decolorization of soluble as well as insoluble dyes is effective	Sludge production
Oxidative Process	Simplicity of application	Agent (H <sub>2</sub> O) requires to be activated
<b>Biological Treatments</b>		
Decolorization by White-Rot Fungi	Using enzymes white rot fungi are able to degrade dyes	Enzyme production is unreliable
Microbial Cultures (Mixed Bacteria)	Decolorization achieved in 24-30 hours	Azo dyes are not readily metabolized under aerobic conditions
Anaerobic Textile Dye Bioremediation Systems	Allows azo and other water soluble dyes to get decolorized	Anaerobic breakdown produces hydrogen sulfide and methane

Table 8 Chitosan composites and adsorption capacity

Adsorbent	Adsorbate	Adsorption Capacity (mg/g)	References
Magnetic $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /Crosslinked Chitosan Composite	Methyl Orange	29.50	[87]
Ethylenediamine-Modified Magnetic Chitosan Nanoparticles	Acid Orange 7	1215.0	[88]
$\beta$ -Cyclodextrin-Chitosan Modified Fe <sub>3</sub> O <sub>4</sub> Nanoparticles	Methyl Blue	2780.0	[89]
Hydroxyapatite/Chitosan Nanocomposite	Congo Red	769.0	[90]
Magnetic Chitosan-Fe(III) Hydrogel	C. I. Acid Red 73	294.5	[91]
Ethylenediamine-Modified Magnetic Chitosan Nanoparticles	Acid Orange 10	1017.0	[88]
Zinc Oxide Nanoparticles/Chitosan	Direct Blue 78	34.5	[92]
Zinc Oxide Nanoparticles/Chitosan	Acid Black 26	52.6	[92]
Chitosan/Organo-Montmorillonite Nanocomposites	Congo Red	290.8	[93]
Fe <sub>3</sub> O <sub>4</sub> /ZrO <sub>2</sub> /Chitosan	Amaranth	99.6	[94]
m-CS/PVA HBs	Congo Red	470.1	[95]



Ethylenediamine Modified Chitosan Nanoparticles	Acid Orange 7	1215	[88]
Ethylenediamine Modified Chitosan Nanoparticles	Acid Orange 10	1017	[88]
Chitosan Coated Magnetite Nanoparticles	Reactive Yellow 145	70.10	[96]
CPAC (Coir Pith Activated Carbon)/Chitosan/SDS (Sodium Dodecyl Sulphate)	Malachite Green	4.8	[97]
Fe <sub>3</sub> O <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub> /Chitosan Composite	Methyl Orange	416	[98]
Chitosan–MgO Composite	Methyl Orange	60	[99]
Chitosan/Polyvinyl Alcohol/Zeolite Electrospun Composite	Methyl Orange	153	[100]
Z-AC/C Composite Beads (Activated Oil Palm Ash Zeolite/Chitosan Composite)	Methylene Blue	151.51	[101]
Z-AC/C Composite Beads (Activated Oil Palm Ash Zeolite/Chitosan Composite)	Acid Blue 29	212.76	[101]
N,O–Carboxymethyl Chitosan/Montmorillonite Nanocomposite	Congo Red	74.2	[102]
Poly HEMA–Chitosan–MWCNT Nanocomposite	Methyl Orange	416.7	[103]
CS–AL (Aliquat-336 Impregnated Chitosan Beads)	Alizarin	126.58	[104]
CS–AL (Aliquat-336 Impregnated Chitosan Beads)	Methyl Orange	42.55	[104]
Chitosan/ZnO Nano-Rod Composite (CS-ZnO)	Alizarin Red S	111.11	[105]
Bentonite/Chitosan@Co <sub>3</sub> O <sub>4</sub>	Congo Red	303	[106]
(CB[8]-CS (Cucurbit [8] Uril onto Chitosan)	Reactive Orange 5	1622.7	[107]
(CB[8]-CS (Cucurbit [8] Uril onto Chitosan)	Acidic Blue 25	1172.7	[107]
(CB[8]-CS (Cucurbit [8] Uril onto Chitosan)	Reactive Yellow 145	1361.9	[107]
Chitosan Hydrogel/SiO <sub>2</sub>	Remazol Black B	0.081±0.004	[108]
Chitosan Hydrogel/SiO <sub>2</sub>	Erythrosine B	0.080±0.005	[108]
Chitosan Hydrogel/SiO <sub>2</sub>	Neutral Red	0.88±0.02	[108]
Chitosan Hydrogel/SiO <sub>2</sub>	Gentian Violet	0.17±0.02	[108]

Table 9 Polyaniline Composites and Adsorption Capacity

Adsorbent	Adsorbate	Absorption Capacity (mg/g)	References
Polylactic Acid/Activated Carbon Composite Bead	Rhodamine B	149.57	[109]
Polylactic Acid (PLA)-Based Cerium Dioxide (CeO <sub>2</sub> )-Graphene Oxide (GO)	Methyl Orange	272.776	[110]
Polyaniline-Coated nylon-6 Nanofibers	Methyl Orange	370	[111]
Polyaniline Fe <sub>2</sub> O <sub>3</sub> Nano-Composite	Acid Violet 19	7.7	[112-113]
Surfactant Doped Polyaniline/Multi Walled Carbon Nanotubes Composite	Brilliant Green	434.78	[114]
Polyaniline Nano Composite	Reactive Dye	143.59	[113]
Polyaniline Lignocellulose Composite	Congo Red	1672.5	[115]
Sugarcane Bagasse Composite with Polyaniline	Congo Red	90.20	[116]

Polyaniline/Saw Dust	Eosin Y	5.9	[117]
Polyaniline/Saw Dust	Methyl Orange	1.37	[118]
Polyaniline/Chitosan	Congo Red	322.58	[119]
Polyaniline/Chitosan	Coomassie Brilliant Blue	357.14	[119]
Polyaniline/Chitosan	Remazol Brilliant Blue R	303.03	[119]
Polyaniline/Starch Nanocomposite	Reactive Black 5	0.81	[120]
Polyaniline/Starch Nanocomposite	Reactive Violet 4	0.83	[120]
Polyaniline/Extracellular Polymeric Substances	Reactive Orange 16	0.4748	[121]
Polyaniline/Extracellular Polymeric Substances	Reactive Brilliant Blue R	0.5775	[121]
Polyaniline/Zirconium (IV) Silicophosphate Nanocomposite	Methylene Blue	12	[122]
Polyaniline/ZrO <sub>2</sub>	Methylene Blue	77.51	[123]
Polyaniline/Heulandite	Light Green SF	69.4	[124]
Polyaniline/Chitosan	Tartrazine	584.0	[125]
Polyaniline/ <i>Tectona grandis</i> sawdust	Crystal Violet	263.2	[126]
polyaniline-tin(II)molybdophosphate Nanocomposite	Malachite Green	78.97	[127]
Polyaniline-g-Hydrolyzed Pectin	Rhodamine B	6.289	[128]
Polyaniline-g-Hydrolyzed Pectin@CdS	Rhodamine B	5.93	[128]
Polyaniline-g-Hydrolyzed Pectin @ Modified CdS	Rhodamine B	35.84	[128]

## 5. Conclusion

This review paper indicates that adsorption using chitosan and polyaniline composites is becoming a promising kind, alternative to replace conventional adsorbents in removing dye. Since there are a variety of chitosan based adsorbents (chitosan derivatives, chitosan composites, chitosan hydrogel, chitosan nanoparticles, etc.) arguments on which type of adsorbent is better is still going on. Besides such two phase (chitosan and cellulose) based composites, researchers also successfully developed multiphase containing materials with better functional properties, such as, polyvinyl alcohol in combination with nano-cellulose and chitosan resulted in composite material with high affinity towards heavy metal absorption. Furthermore, blends of chitosan resulted in material with anti-bacterial activity, metal ions adsorption, odor treatment properties etc. Commonly used methods for blending are electro-spinning, casting and sol-gel transition. This review proposed that chitosan/hydrogel/SiO<sub>2</sub> prepared by sol-gel method showed minimum adsorption capacity 0.080±0.005 because the mechanism involved for dye adsorption was found to be lower energy physical adsorption interaction. The study also concluded that biodegradable polymer composite, β-cyclodextrin-chitosan modified Fe<sub>3</sub>O<sub>4</sub> nanoparticles recorded highest adsorption capacity of 2780 mgg<sup>-1</sup> for removing methyl blue dye. The reason for the high adsorption capacity relates to the spherical shape of polymer. Spherical molecular polymers have large surface area, indicating that large number of effective sites could exist in the surface to adsorb the MB molecules in aqueous media. Therefore, it can be utilized as environment friendly bio-adsorbent for the removal of dyes from aqueous solution due to efficient and fast adsorption process. Despite, *Sajid et al., 2018*

extensive research in field of chitosan based cellulose/nano-cellulose composites their commercial applicability is still limited this might be due to their uneconomical production procedure and poor properties as compared to synthetic counter parts.

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