



Article Review

Textile dyes removal from wastewater using recent promising composites: A review

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ABSTRACT

Dyes are widely used in many fields such as textiles, leather, paper, and plastics. The industries which used dyes consume a large amount of water, and in some textile dyeing operations, as much as 15-20% of dyes used do not attach to the fibers, so they are lost to wastewater, and the resulting colored effluents can represent a serious water pollution problem due to their color content and toxic components which, over time, are directly involved in the degradation of our ecosystem. The usual effluent treatment involves biological systems like activated sludge; however, conventional treatment has not efficiently removed the effluent dye due to the recalcitrant nature of the dyes and the diverse composition of the effluent. Some conventional methods which have been largely used to eliminate dyes ions from various industrial effluents are often costly, especially in removing dye ions from dilute solutions. Adsorption is considered quite attractive in terms of its efficiency of removal from dilute solutions. Recently, various composites have received wide attention due to their outstanding properties in wastewater treatment. However, non-biodegradable synthetic polymers are largely applied as the organic components of these composites, leading to negative environmental impacts.

In this paper, after a brief description of textile dyes, their toxicity and the conventional physic-chemical processes used in the degradation of dyes, we have focused on some of the work published over the past 5 years using the most promising composites for environmental purposes. Overall, the biopolymers and magnetic-based composites have demonstrated outstanding removal capabilities for a large range of dyes.

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1. Introduction

Pollution is a very complex phenomenon. It affects all urban areas, rural areas, and the aquatic environment to varying degrees. This pollution undoubtedly contributes to the retrogression of the environment and the damage to human health. Water pollution appears when materials are spilled into the water and degrade its quality. It includes all

superfluous matter which cannot be destroyed by water naturally. In other words, any material added to water that is beyond its capacity to destroy it is considered pollution. Pollution can, in certain circumstances, owing to nature itself, such as the case of the flow of water through soils with a high level of acidity. However, most of the time, it is human actions that pollute the water. Two types of

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pollution sources exist. Specific sources and unspecified sources, precise sources include factories, sewage treatment plants, septic systems, and other sources that very clearly discharge pollutants into waterways. Unspecified sources are hard to find since the difficulties of tracing them from a precise location. They include sediment flows like fertilizers, chemicals, farm animal waste. Landfills can also be an unspecified source if site substances filter the waste into water supplies. In the present study, we were interested in a specific source of wastewater which is dyes wastewater.

The textile and tannery industries are the industries that consume the most water. After their activities, the quantities of wastewater release are very large, which generates severe water pollution. Depending on a report published in 2000 by the Textile Industries Federation, the consumption of dyes in this sector in Algeria exceeds 4012 tons annually; the consumption of auxiliary chemicals reaches 16,356 tons/year. Wastewater from the textile industry has become a real health and environmental problem because not only does it make aquatic environments unsightly and dangerous, but certainly pollutes drinking water. It is very recommended that textile effluents must be treated before being released into receiving environments.

Dyes can damage photosynthetic activity owing to decreased light penetration, they can also be dangerous to some aquatic species due to their compositions (presence of metals and hydrocarbons...). They are also carcinogenic in various species. They can also cause serious problems in humans with the kidney, reproductive system, liver, brain, and central nervous system. Azo dyes are toxic due to the presence of toxic amines in the effluent. Likewise, anthraquinone dyes are very resistant to degradation and the color remains for a long time in the effluent. Reactive dyes are chemically stable, little degradable, and soluble in water causing serious damage to the environment.

Recently, a great interest has been observed in wastewater treatment using single or hybrid processes such as adsorption, chemical oxidation, photocatalysis, membrane separations, ultrasound, optical and electrochemical processes...

Although traditional materials are still being experimented with some conventional wastewater treatment methods, the use of novel materials such as composites is gaining popularity. When discussing the histological treatment of wastewater. The present paper aims to provide an overview of new promising composites that are used with success to degrade dyes present in wastewater, which are considered the main sources of environmental pollution.

2. Textile dyes

Dyes are materials having the property of coloring another on which it is fixed. Color concentration has a relation with the selective energy absorption by certain

groups of atoms called chromophores. The more easily the chromophore group gives an electron, the more intense the color.

The chromogen atom can change color or increase its intensity due to the chromophore. They are called auxochromatic groupings. Chromophores are conjugated π -bonded entities or transition metal complexes. Combinations of molecular orbitals are a way to differentiate dyes from each other. The coloring corresponds to the possible transitions after absorption of light radiation between these energy levels specific to each molecule.

Dyes can be natural or synthetic and it is used to give a durable coloring to a material, or to color certain food. They have two specific properties: color and the ability to be fixed to solid substrates such as textiles, by dyeing or printing techniques.

Dyes are widely used in several industrial fields, they are used to color paints, plastics, textiles [2, 3], leather [4], seeds, cement, coatings, wood, etc. The use of dye is known also in the food industry [5, 6]. In addition, they can be used in research [7], to reveal small transparent structures by microscopy. There are only about ten natural dyes, but several thousand synthetic dyes.

3. Classification of textile dyes

The textile industry contains hundreds of dyes; the majority of them are toxic. They generate serious pollution that is difficult to control.

The classification of dyes can be made in different ways but the most used is by the chemical constitution (azo dyes, anthraquinone, triazin, methine, indigoid, etc.). If this classification is of interest to the manufacturer of dyestuffs, the finisher (dyer) prefers the classification by field of application as follows: mordant dyes, acid dyes, metallic dyes, direct dyes, cationic dyes, sulfur dyes, reactive dyes, dyes azo, oxidation colors and plastisoluble dyes.

Table 2. gives the classifications of dyes according to the chemical structure and an example of each class.

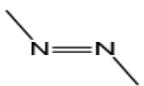
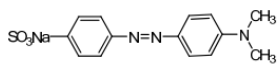
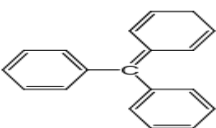
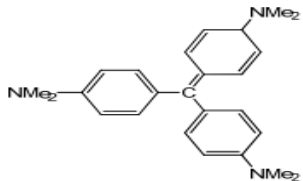
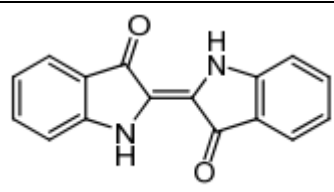
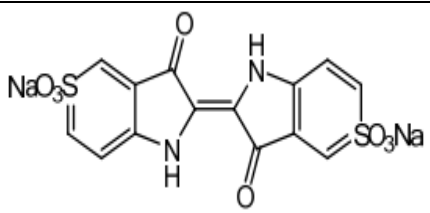
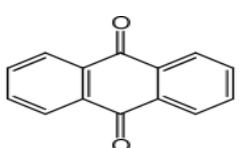
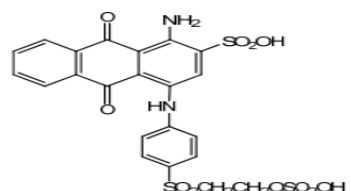
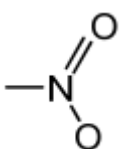
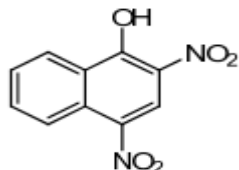
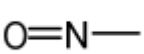
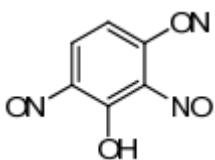
4. Dyes toxicity

Wastewater from several industries such as textiles, paper, printing, plastics, food, and cosmetics cause very serious environmental problems [9]. Owing to their high production and widespread application, synthetic dyes are a source of an environmental impact and represent a very serious risk factor for public health. The dyes are rejected in significant proportions between 10 and 15% [10].

Table 1. Main chromophoric and auxochromatic groups, classified by increasing intensity [1].

Chromophoric Groups	Auxochromatic Groups
N = N: azo group	NH ₂ : Amino
N = O: nitroso group	NHCH ₃ : Methylamino
C = O: ketone or carbonyl group	N (CH ₃) ₂ : Demethylamino
C = C: vinyl group	OH: Hydroxyl
C = S: thio carbonyl group	OR: Alkoxy
C = S: Sulfide Electron donor groups	Electron donor groups

Table 2. Classification of dyes according to the chemical structure [8, 9].

Chemical classes of dyes	Chromophore	Example
Azo dyes		 Methyl orange
Trimethylmethane dyes		 Basic violet
Indigo dyes		 Acid blue 71
Anthraquinone dyes		 Reactive blue 19
Nitro dyes		 Acid yellow 24
Nitroso dyes		 Fast green O

In industrial effluents, dyes represent the most dangerous chemical component. Since their presence in water bodies cause several issues, for example, owing to the high color intensity and the visibility of the basic dyes even in very low concentrations, a decrease in the light penetration can be observed which affect photosynthetic activity due to the decrease in light penetration and can also be toxic to some aquatic species due to the presence of metals and hydrocarbons [11]. They can also cause serious problems in humans with the kidney, reproductive system, liver, brain, and central nervous system [12].

The toxicity of the Azo dyes is owing to the existence of toxic amines in the effluent. Likewise, anthraquinone dyes remain for a long time in the effluent, they are shown great resistance to elimination through the different processes.

Reactive dyes are very stable, little degradable, and soluble in water causing serious damage to the environment [8]. They are also aesthetically objectionable for drinking and other purposes [13]. Dyes can cause allergy, dermatitis, skin irritation [14], and also provoke cancer and mutation in humans [15].

Several research studies on the toxic effects of dyes on healthy humans have been developed. Indeed, researchers have shown that amino dyes are often apt to cause skin irritation and dermatitis. Similar effects with the production of eczema and ulceration have been observed in factory workers in the manufacture of dyes of the triphenylmethane series. Allergic reactions, asthma sometimes and especially eczematous dermatitis have been observed with various dyes azo amines, anthraquinones, as well as certain dyes from the group of Naphthalenes [16, 17].

5. Conventional processes used in the degradation of dyes

During the various dyeing stages, more or less significant amounts of dyes are lost due to a lack of affinity with the surfaces to be dyed or colored. These organic discharges are toxic as we have already mentioned and require an adapted depollution technique. The treatment of textile waste, taking into account their heterogeneity of composition, will always lead to the design of a treatment chain ensuring the elimination of the various pollutants in successive stages.

The first step consists of eliminating the insoluble pollution by means of pretreatments (screening, grit removal, oil removal) and/or physical or physicochemical

treatments ensuring a solid-liquid separation. According to some researchers Barclay and Buckley [18], the depollution techniques most often involved in the second stage in the textile industries are divided into three types: physical, chemical, and biological. So, there are a number of techniques for cleaning up polluted water produced by industrial sectors. In general, different combinations of processes make it possible to effectively treat industrial contaminations. However, these methods have an increasingly high cost so there is a growing interest in developing efficient and low-cost methods.

Several methods for the treatment of wastewater such as coagulation and others have been effectively applied for the removal of different dyes from aqueous solutions, the advanced oxidation process [19, 20], adsorption [21–25], photocatalysis [26–28], and aerobic or anaerobic digestion [29–33].

5.1. Treatment by physical methods: membrane filtration

Membrane filtration controlled by hydraulic pressure is available in microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. The effluent passes through a semi-permeable membrane that retains upstream contaminants larger than the diameter of the pores. It allows the separation of pollutants from the water, the generation of a purified aqueous effluent [34]. Of the four types of process, nanofiltration and reverse osmosis are the most suitable for the partial reduction of color and small organic molecules, but reverse osmosis remains the most common [35].

Membrane technology used to degrade pollutants in contaminated water has great complexity. These processes, which are limited in their applications, require significant capital investments and the reprocessing of the concentrate is up to six times more expensive than that of the original effluent. Besides the high cost of these installations, the membranes are not able to resist certain types of chemicals and certain pH values and are deteriorated especially by the presence of microorganisms [36].

The disadvantages of the membrane filtration process could be summarized in the following points: the process scaling for different flow rates, low life rate, and their application to only feed rates with low pollutant concentrations. In addition, energy consumption increases with increasing concentrations of pollutants and requires labor which must be highly skilled and therefore expensive.

5.2. Treatment by physico-chemical methods

5.2.1. Coagulation–flocculation

The term coagulation-flocculation is understood to mean all the physicochemical processes by which colloidal particles or solids in fine suspension are transformed by chemical flocculants into more visible and separable species (flocs). The flocs formed are then separated by settling and filtration and then discharged. Inorganic coagulants such as alum (aluminum potassium sulfate) give the most satisfactory results for the discoloration of textile effluents containing disperse vat and sulfur dyes but are totally ineffective for reactive, azo, acids, and basics dyes [37]. Furthermore, coagulation-flocculation cannot be used for dyes that are highly soluble in water. Large quantities of sludge are formed with this process and their regeneration or reuse remains the only way out and requires additional investments.

5.2.2. Adsorption

Adsorption is the process in which molecules in a fluid (gas or liquid), called an adsorbate, attach to the surface of a solid, called adsorbent. By the surface of the solid, we mean the external and internal surfaces generated by the network of pores and cavities inside the adsorbent. There are two types of process adsorption: physical adsorption or physisorption and chemical adsorption or chemisorption as shown in Figure 1.

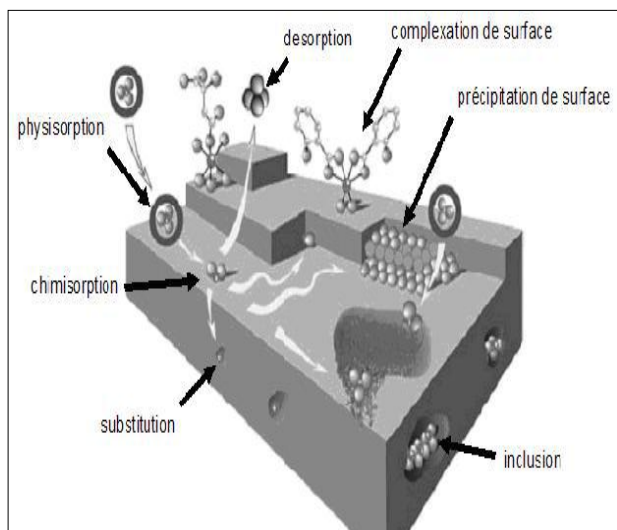


Fig 1. Main interactions between an atom or a molecule and a solid at the interface adsorbent/adsorbate [38].

In the case of physical adsorption, the fixation of the adsorbate molecules on the adsorbent surface is done essentially by the Van der Waals forces and the forces due to the electrostatic interactions of polarization, dipole, and quadrupole for adsorbents having an ionic structure.

Physical adsorption occurs without changing the molecular structure and is perfectly reversible (i.e.

adsorbed molecules can be easily absorbed by lowering pressure or increasing temperature).

In the case of chemical adsorption, the process results from a chemical reaction with the formation of chemical bonds between the adsorbate molecules and the adsorbent surface. The binding energy is much stronger than in the case of physical adsorption and the process is much less reversible and even sometimes irreversible.

5.3. Treatment by chemical methods

Chemical oxidation techniques are generally applied for hazardous organic compounds degradation that presents in low concentrations, in pretreatment before biological processes, wastewater purification loaded with constituents resistant to biodegradation methods, and in post-treatment to reduce the aquatic toxicity [39].

The two reagents most often used for this type of treatment are Hydrogen peroxide and Chlorine. Hydrogen peroxide is considered a strong oxidant, its application for pollutants degradation is well established. But oxidation alone by Hydrogen peroxide is not sufficiently effective for high concentrations of dye. Hamada et al. have proposed to treat azo dyes with sodium hypochlorite, but even if the initial molecule is destroyed, the halogens are likely to form trihalomethanes which are carcinogenic to humans with the degradation byproducts [40].

5.4. Treatment by biological methods

By biological water purification is meant the decomposition of organic pollutants in water by microorganisms. Biological processes fall into two categories: aerobic treatments and anaerobic treatments.

5.4.1. Aerobic treatment

The pollutants are broken down in a biological unit consisting of a pool of sludge activated by aerobic bacteria and other microorganisms into a sludge that settles. Ideally, organic pollutants are oxidized to carbon dioxide. After purification, the sludge is separated from the wastewater by sedimentation in a settling tank. A part is recycled and the surplus is removed after pressing or centrifugation.

5.4.2. Anaerobic treatment

Unlike aerobic biodegradation, anaerobic digestion of organic compounds occurs in the absence of oxygen and forms carbon dioxide, methane, and water. It is an efficient process for the treatment of waste very loaded with organic matter and the methane formed can be used as heating energy. The reduction conditions in anaerobic digestion are suitable for the discoloration of azo dyes by cleavage of the azo bond resulting in the subsequent destruction of the

chromophore group, but complete mineralization is not possible in this type of process. Degradation of the original molecules often results in the formation of more toxic amines than the original molecule, which ends up in shallow aquifer sediments and groundwater. Conventional bioprocessing methods have no effect on most synthetic dyes due to their complex polyaromatic structure and refractory nature. Venceslau et al. have estimated the reduction in staining by biological methods to be only 10–20% [41].

6. Recent promising composites used in the degradation of dyes

The literature is rich in published works in the dyes degradation field; various materials have been tested in the decontamination of dyes or real treatments on a pilot scale in laboratories or at an industrial scale. The synthesis and the use of various types of materials is a focus of strategic research for many research teams in the scientific community.

Among the materials that have shown great popularity for dyes removal; the activated carbon [42–44], zeolites [45–48], and sawdust [49–51]...

In particular, natural-derived polymers have got wide attention in the preparation of green composites (fully biodegradable).

Researcher and industries have focused their efforts on the development of natural-derived polymers due to their remarkable properties such as biodegradability, low-cost, abundant...

The family of polysaccharides are polymers composed of several "oses" linked together by "osidic bonds", they are carbohydrate macromolecules formed by linking together many elemental sugars of plant or animal origin. The most common polysaccharides are cellulose, starch, and algae, of plant origin, as well as chitin which comes from numerous animal species or fungal.

These biopolymers constitute an interesting and attractive alternative within the framework of the replacement of polymers from petrochemicals and are already the subject of several industrial applications. They are particularly used as adsorbents due to their structure particularly, chemical stability, high reactivity, and selectivity towards dyes, resulting from the presence of chemically reactive groups in their structural chains.

Figures 2, and 3 show, respectively, the structure of polysaccharides, chitin, chitosan, and alginate.

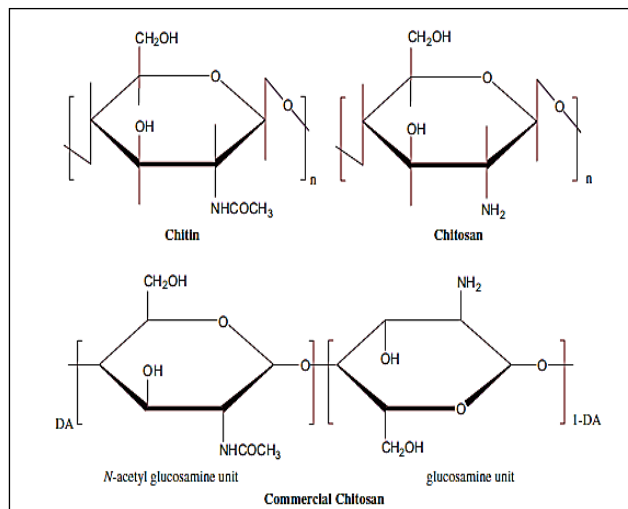


Fig 2. Chemical structure of chitin [poly(N-acetyl-b-D-glucosamine)], chitosan [poly(D-glucosamine)] and commercial chitosan (a copolymer characterized by its average degree of acetylation (DA)) [52].

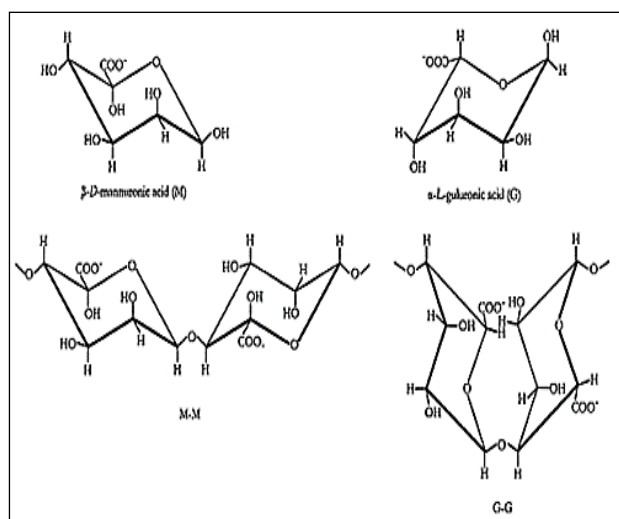


Fig 3. Chemical structures of mannuronic (M) and guluronic (G) acid monomers and their secondary structure as blocks (MM and GG) in the alginate chain [53].

In addition, it is well known that polysaccharides, which are derived from abundant, renewable, and biodegradable resources, have a tendency to associate, through physical interactions and chemicals, with a wide variety of molecules, thus expanding the range of their use in several fields. Therefore, adsorption on polysaccharide derivatives can be an inexpensive and efficient procedure in the decontamination of polluted water, and an indispensable tool for the protection of the environment.

In fact, the development of commercial applications for chitin and chitosan, algae, and alginate progressed. Emphasis on environmentally friendly technology has

stimulated interest in these biopolymers, which are versatile biodegradable and less toxic than their synthetic equivalents.

The presence of chemically reactive groups (hydroxyl functions, carboxyl, acetamide, or amine) in the chains of these biopolymers justified the interest in their use in the field of biosorption and treatment of industrial wastewater. Many approaches have been studied and modified for the development of these materials, in order to adapt them to the requirements of the chemical industry.

These kinds of biopolymers have many unique advantages and characteristics such as abundance, non-toxicity, biocompatibility, reactivity, biodegradability, and their effectiveness for the treatment of dye contaminants.

6.1. Alginate derived composites

Alginate is a polysaccharide produced by brown algae and bacteria. Alginic acid was discovered, extracted, and patented for the first time by Stanford (1881). The polysaccharide has been identified as a structural component of marine brown algae, where it constitutes up to 40% of the dry matter and occurs mainly in the intercellular mucilage. Extraction of alginate from algae is based on the water solubility of this polymer: alginic acid is insoluble in water, but it is soluble in salts of monovalent cations such as sodium Na^+ or potassium K^+ . Thus, changes in pH allow its purification and separation from other components [54].

6.1.1. Pure alginate beads

The adsorption of dyes on alginate beads has also been widely studied; Hassan et al. have prepared and characterized calcium alginate composite for the adsorption of methylene blue [55]. The elimination of methyl orange [56], and malachite green [57], by calcium alginate beads, have been characterized by adsorption depending on several factors such as the effect of the initial concentration, the effect of the dose, the temperature, and the study of the isotherm.

The removal of Basic black dye from colored effluents in dynamic batch mode has been studied by Aravindhan et al. using calcium alginate composite. The potential use of Basic black dye is much known in the leather industry. Several parameters that affect the dye adsorption have been investigated and optimized conditions have been determined. The maximum adsorption capacity of 57.70 mg/g was found at an initial dye concentration of 300mg/L, with 4 g/L of alginate dosage, at pH 4.0 and at room temperature (30 ± 1 °C). Adsorption isotherm studies clearly

indicate the effectiveness of the use of alginate beads in the removal of Basic black dye [58].

The elimination of cationic and anionic dyes such as methylene blue and methyl orange on alginate composites studied by Rocher et al. revealed that the adsorbed amount of the dyes was 0,62 and 0,68 mmol/g respectively [59].

Malachite green, Methylene blue, and Crystal violet dyes were also removed on alginate beads and the adsorbed amount was found to be 248.78, 466.60, and 456.52 mg/g respectively [60]. The adsorbed amount of Crystal violet found by Elwakeel et al. was 0.13 mmol/g at 25 ± 1 °C [61].

6.1.2 Bentonite-alginate composites

Recently, alginate and its derivatives have deserved very special attention. A number of articles have demonstrated the effectiveness of alginate for the elimination of a large range of dyes. Lezeharia et al. have used Algerian bentonite bridged by aluminum and modified by a surfactant. These two clays were encapsulated by the alginate to obtain different composites. This study aimed to develop an adsorbent for the elimination of cationic dye (safranin) in aqueous solutions. Series of experiments were carried out to test the adsorption capacities. The results showed that the prepared composites can remove successfully the dye. The maximum adsorption capacity of the composite materials for the dye deduced from the Langmuir absorption isotherm is 706 $\mu\text{mol/g}$ for the composite bridged bentonite-alginate 705 $\mu\text{mol/g}$ for the bridged bentonite composite modified by a surfactant-alginate [62].

Hassani et al. have studied the cleanup of basic red 46 by the montmorillonite-alginate nanobiocomposite. The percentage of dye removal was found to be 85.07 % obtained for an initial dye concentration of 30 mg/L, at a dose of 2 g/L, a contact time of 60 minutes and, a temperature of 25 °C. The adsorption capacity decreases with decreasing pH and the initial mixing speed. The pseudo-second-order kinetic model describes the results well ($R^2 = 1$). Based on the Langmuir isotherm model, the maximum adsorption capacity is approximately 35 mg/g [63].

In addition to these results, many kinds of promising composites of alginate-bentonite have been tested with success in the treatment of Basic blue 9 [64], Acid green B and Direct pink 3B [65], Crystal violet [66], Methyl orange [67], Congo red [68], Methylene blue [69].

Alginate (polycarboxylic biopolymer), bearing guluronic and mannuronic acid groups, has been modified in different research work either by crosslinking in order to

improve their chemical stability or functionalization by grafting of specific reactive groups to enhance their efficiency towards dyes removal [70-74].

Regarding alginate, new forms of beads crosslinked using Tripolyphosphate (TPP) have been used to produce more rigid balls. However, the crosslinking takes place more often by polyethylenimine (PEI) and bis-polyoxyethylene bis [amine] (PEGA) for the synthesis of alginate-poly-L lysine [75], as well as poly (vinyl alcohol) (PVA) and poly (acrylic acid) (PAA) for the synthesis of modified alginate gels [76]. Crosslinked or/and grafted materials have several characteristics and properties which enhance the removal of dyes.

6.1.3. Activated carbon-alginate composites

Different studies report the elimination of dyes using activated carbon-alginate composites; Kwak et al., have studied the removal of methylene blue dye on Sericin-derived activated carbon-loaded alginate composite, the prepared composite had shown effectiveness for methylene blue removal, with an adsorption capacity of 502.5 mg/g. regeneration studies have shown great stability of the composite during 5 cycles of the adsorption-desorption process [77].

Hassan et al. have studied the removal of methylene blue on alginate beads containing activated carbon. The adsorption was performed on the activated carbon powder made from coconut shells, the alginate beads, and the activated carbon alginate composite. The porosity, area, and total pore volume of these materials have been classified as follows: the coconut shells > the activated carbon alginate composite > the alginate beads. The methylene blue adsorption isotherms on the above adsorbents were modeled by the Langmuir equation. The adsorption capacity of materials was given in this order: coconut shells (1030)> activated carbon alginate composite (892)> alginate beads (800 mg/g) [55].

In addition, Annadurai et al. have prepared and characterized the alginate beads in which commercial activated carbon powder was encapsulated for the adsorption of Rhodamine 6G. In this study, several factors were studied: the concentration of the dye from 100 to 300 mg/L, the pH 7-9, and the temperature of 30-60 °C. High adsorption percentages of rhodamine 6G were obtained using the activated carbon-alginate composite [78].

Lin et al. have studied the adsorption of organic pollutants by activated carbon-alginate composite prepared using different types of metal ions with different charges and sizes. Quantitative analyzes have shown that a large part of adsorption of positively charged compounds as well

as low molecular weight and electrically neutral compounds such as p-chlorophenol have been attributed to the activated carbon-alginate composite prepared in a solution of CaCl_2 . However, the high molecular weight humic acid was not adsorbed. However, positively charged compounds, such as methylene blue were adsorbed more strongly on the composite prepared with low calcium concentrations [79].

The team of Li et al. was able to use composite fibers of calcium alginate and carbon nanotube with different ratios for the removal of methyl orange. The results of this study confirm that the addition of the carbon nanotube could increase the adsorption capacity of methyl orange. The maximum adsorption capacity of the composite deduced from the Langmuir isotherm is 14.13 mg/g with a quantity of high carbon nanotube of 25% by weight percentage [80].

6.1.4. Graphene oxide-alginate composites

The Graphene oxide and alginate composites have shown a great potential of dyes removal from wastewater. Li et al. have successfully prepared the graphene oxide and alginate composite hydrogels for adsorption of methylene blue [81].

Xiao et al. have synthesized a hybrid composite using alginate and graphene oxide. The composite hydrogels exhibited improved dye adsorption performance, especially for cationic dyes. In the regeneration study, the composite has shown great stability for the adsorption of the dye. After 10 cycles of adsorption-desorption, the composite has eliminated more than 90% of dye. The found results by Xiao et al. have shown a promising composite which used with success for environmental purposes [82].

Simultaneous adsorption of coexisting organic dyes from industrial wastewater was investigated by Bai et al. using alginate hybridized with graphene oxide for the removal of methylene blue and neutral red in both single and binary systems [83].

The removal of Methylene blue dye on the composite of alginate-Graphene oxide has been widely studied by other researchers [84-86].

6.1.5. Biosorbent-alginate composites

Several works have been recently published on the elimination of a large range of dyes using Biosorbent-alginate composites. Table 3, illustrates the most recent works. As shown the Table 3, composites made from biosorbent and alginate have shown great results for the elimination of cationic dyes such as methylene blue, methyl violet, crystal violet, malachite green...

Table 3. Alginate-bioadsorbents based composites for the removal of synthetic dyes from aqueous solution.

Alginate-based composite	Dyes	Removal capacities (mg/g)	pH	T (°C)	References
Activated-lemon-peels/alginate composite	MB	841,37	6.5	24	[87]
α -keratin/ Alginate	MB	409.48	5	25	[88]
Alginate-coated perlite	MB	104.1	/	/	[89]
	MG	74.6			
	MV	149.2			
ball-milled biochar-calcium alginate composite	MB	1210.7	5	25	[90]
alginate-kelp biochar composite	CV	1989.55	/	30	[91]
Acetic acid activated Citrus peels and calcium alginate composite	MB	923	6.5	24	[92]
	CV	881	5.9		
Sugarcane bagasse biochar Calcium-alginate	MB	71,21	7,4	/	[93]

In literature, there are a huge number of publications for the removal of cationic dyes using several kinds of composite basically made from alginate. However, few researches have investigated the elimination of anionic dyes using alginate-based composite. Most of them have found that these kinds of composites are not suitable for the elimination of anionic dyes owing to the repulsion between the carboxylate group of the alginate and the negative form of anionic dyes [68].

6.2. Chitosan derived composites

Chitosan, also, owing to its characteristics related to its structure has been widely studied as a low-cost adsorbent for the treatment of effluents of dyes industries. Significant works on the treatment of textile effluents by chitosan derivatives have been carried out by different researchers, they indicated that the crosslinked chitosan beads can be used for the removal and recovery of different kinds of dyes such as reactive red 189 [94, 95], Reactive orange 16 [96], Crystal violet [97], methylene blue and rhodamine B [98].

Chiou et al. have studied the adsorption of various dyes reactive dyes (Reactive Blue 2, Reactive Red 2, Reactive Yellow 2, Reactive Yellow 86), acid dyes (Acid Orange 12, Acid Red 14, Acid Orange 7), and direct dye (Direct Red 81) by chitosan [99].

Other researchers have targeted the treatment of anionic and cationic dyes on chitosan-based adsorbents [100].

Other studies have confirmed that chitosan has an exceptional adsorption capacity towards Orange II in a single system and coexisted with methylene blue in binary system dyes [101].

The advantages of using bio-adsorbents like alginate and chitosan are the possibility of making chemical modifications, ease of use on a laboratory scale, shaping

varied, biodegradability, biocompatibility, and the use at several pH ranges.

Chitosan and alginate are versatile and can be easily packaged to prepare products of different shapes, such as powder, thread, membrane, film, nanoparticle, beads, fibers, and hollow fibers, granular, resin, flake, sponge, etc. Figure 4 shows some forms commonly used chitosan and alginate.

Chitosan and alginate have a great ability to chelate metal ions compared to other natural polymers; this property depends on their physical state and their chemical aspect.

However, by comparing the two polysaccharides, chitosan has binding capacities more efficiently due to the richness of its structure in amine functions which make it possible to form complexes with most toxic metals. The high percentage of nitrogen, in the form of amine sites, are the main groups reactive to metal ions and are responsible for binding by chelation mechanisms.

However, alginate has demonstrated the great utility and extended potential as a biomaterial. For many biomedical, food, and beverage applications and as an effective adsorbent for the treatment of solutions contaminated with dyes effluents.

Compared to conventional adsorbents, frequently used to eliminate organic pollutants from the solution, such as commercial activated carbons and synthetic ion exchange resins. Dyes removal using polysaccharide-based materials offers several advantages but includes also drawbacks.

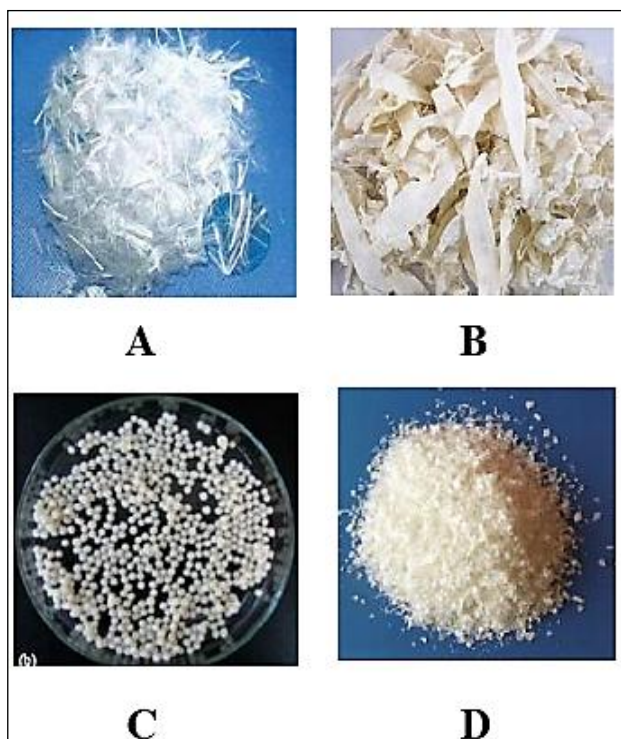


Fig 4. Some forms of the adsorbents prepared on the basis of chitosan and alginate **A)** Fibers; **B)** Flakes; **C)** Beads; **D)** Powder [102].

6.2.1. Pure chitosan composites

There have been several published studies concerning the adsorption of pollutants by chitosan and their composites, some studies of the adsorption of dyes have been investigated the removal of dyes using pure chitosan composites; for example; Bekci et al., have studied the adsorption of malachite green by chitosan beads. The results of these studies showed good adsorption of the dye by the chitosan beads with a percentage elimination of 99% at pH = 8.

The adsorption data of the dye to the chitosan beads were represented by the Langmuir and Freundlich equation. The Langmuir model presents the best correlation coefficients. The adsorption capacities of Malachite green are 93.55 mg/g at 303 K; 74.83 mg/g at 313 K; 82.17 mg/g at 323 K [103].

The adsorption of anionic dyes in water by chitosan beads crosslinked with glutaraldehyde has been studied by Cestari et al. Crosslinked beads have also been used for the removal of reactive dyes; yellow, blue, and red at pH = 2. The beads of the chitosan have shown that the adsorption capacity of reactive yellow increases with the temperature increasing from 25 to 50 °C. In contrast, the adsorption of reactive blue decreases with temperature increasing from 25 to 50 °C. In addition, the adsorption of reactive red

increases from 25 to 35 °C and decreases from 45 to 50 °C [104].

In another work, Chiou et al. have studied the batch adsorption of four reactive dyes, three acid dyes, and one direct dye by chitosan beads chemically crosslinked with epichlorohydrin and sodium tripolyphosphate. The results show very high adsorption capacities to remove anionic dyes, with a maximum monolayer adsorption capacity between 1911 and 2498 g/kg at 30 °C [99].

6.2.2. Bentonite-chitosan composites

Wang et al. used the chitosan-montmorillonite nanocomposite as an adsorbent for the removal of Congo red. Chitosan-montmorillonite nanocomposites were prepared by monitoring the molar ratio of chitosan and montmorillonite. The nanocomposites were characterized by FTIR and XRD. Different effects were studied for the elimination of the dye: the montmorillonite/chitosan molar ratio, the initial pH value, and temperature. The results show that the adsorption capacity of the chitosan-montmorillonite nanocomposite was higher than the average values of those of chitosan alone and montmorillonite alone. The adsorption and isotherm kinetics were also studied. All adsorption processes have been shown to be best matched by the pseudo-second-order equation and the Langmuir equation [105].

For the removal of cationic dyes, Monvisade et al., have used the montmorillonite-chitosan composite. Dye adsorption was performed on sodium montmorillonite, chitosan, and montmorillonite intercalated in chitosan. The results have shown that the montmorillonite-chitosan composite has the greatest adsorption capacity of the order of 46–49 mg/g when the concentration of the initial dye was 500 mg/L, equivalent to 92 - 99% elimination percentage [106].

Autar and Hameed have also studied the adsorption of methylene blue in batch mode and in fixed-bed by the clay-chitosan composite. The following conclusions could be drawn from this Batch mode study: The adsorption characteristics of methylene blue ions are strongly affected by the pH of the initial solution, from the initial concentration of blue ions of methylene, the number of salts, and the temperature. The amount of methylene blue ions adsorbed on the clay-chitosan composite was found to increase with increasing initial BM ion concentration, contact time, and pH of the solution, and it decreases with increasing ionic strength. Fixed bed adsorption capacities increase with increasing initial BM ion concentration and bed height, and decrease with increasing feed rate [107].

Zhang et al., have been studied the adsorption of methyl orange by the crosslinked chitosan-bentonite composite grafted by Zr (IV). The composite was characterized by several techniques: Scanning electron microscopy, X-Ray diffraction, Fourier transform infrared spectroscopy. Series

of experiments were carried out to test the composite adsorption capacity. The maximum adsorption capacity according to the Langmuir model at 303 K was 438.6 mg/g [108]. Table 4. illustrates the use of based chitosan composite for the degradation of dyes.

Table 4. Dyes removal using chitosan based composite.

Chitosan-based composite	Dyes	Removal (mg/g)	pH	T (°C)	Reference
Cross-linked O-carboxymethyl chitosan	CV	239.54	/	/	[97]
Chitosan/Congo red composite Chitosan Solutions	MB	1457.1	6.5	25	[98]
	Rh B	990.0	6.5	25	
	CR	>44956.2	7	25	
Cross-linked chitosan	RRed 2	788.55	2	/	[109]
Functional chitosan composite β -cyclodextrin/chitosan composite	IC	500	4	25	[110]
		1000	4	25	
Magadiite-chitosan composite	MB	45.25	/	30	[111]
	CR	135.77	/	30	
Grafted-crosslinked material g-CCTS	MB	79.09	12	20	[112]
Grafted-crosslinked material Fe-g-CCTS	RBR	918.53	2	20	
Thylenediamine-modified, TEOS-coated magnetized chitosan beads (ETMC)	Cibacron BY3G-P	179.4	2	/	[113]
	Cibacron BR3B-A	377.6			

Table 5. Dyes removal using different magnetic composites.

Magnetic-based composite	Dyes	Removal (mg/g)	pH	T (°C)	Reference
CoFe ₂ O ₄ /chitosan magnetic composite	IB	380.88	3	55	[117]
Magnetic chitosan-luteraldehyde composite	CV	105.467	11	25	[118]
Polyamine-modified magnetic graphene oxide	MV	243	7	25	[119]
	AR88	303	4	25	
AC/CoFe ₂ O ₄ magnetic composite	MB	87.48	/	/	[120]
	MV	83.90	/	/	
	NB	86.24	/	/	
Algal activated carbon/Fe ₃ O ₄ magnetic composite	MB	60.60	7	25	[121]
	MV	59.88	7	25	
Carboxyl-functionalized magnetic composite	MB	43.15	10	25	[122]
Eroferic oxide/polypyrrole magnetic composite	EMO	212.31	/	25	[123]
	BG	149.48 263.85			
Polypeptidylated hemoglobin (Hb)/iron oxide magnetic composite	Eblack-T	217	/	/	[124]
chitosan-based magnetic composite CTS@SnO ₂ @Fe ₃ O ₄	RBR	981.23	2	20	[125]
Anionic polyacrylamide-modify-chitosan Magnetic Composite	CV	2330.17	/	45	[126]
	MB	1044.06			
Magnetic lignin composite	CR	198.24	7	25	[127]
	TY	192.51			
Mesoporous magnetic biochar composite	MG	515.77	/	/	[128]

6.3. Magnetic composites

Recently, magnetic composites have been received great attention in the field of wastewater treatment. Akbarzadeh et al. have described the existence of five basic types of magnetism: diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism, and ferrimagnetism [114].

There are different techniques used for the synthesis of magnetic composites. Magnetic metal oxide composite (powder CuFe_2O_4 and $\text{MnO-Fe}_2\text{O}_3$) was first prepared by a simple co-precipitation method from environmentally friendly and low-cost materials by Wu et al. [115, 116].

Researchers have used the magnetic composite for the removal of a large range of synthetic dyes; some results are given in Table 5.

The results given in Table 5 demonstrate that the prepared magnetic composites developed in the works demonstrate an interesting and promising dyes removal; they have successfully used to remove many kinds of dyes.

7. Conclusion

This review is mainly aimed to assemble current composites made in remediating the synthetic dyes in wastewater. We have focused on a general description of the toxicity of dyes basically used in the textile industry. In addition, we have categorized and explained the main technological processes that are used to remove dyes from water. In the last few years, researchers have focused their efforts on the development of novel composites basically made from biopolymers and from magnetism in order to use them for environmental purposes. These matters have been chosen due to their remarkable properties such as biodegradability, low-cost, abundant...

Bioremediation of dye-based wastewaters using composites has shown satisfying results for the removal of different kinds of dyes from wastewater.

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Conflict of Interest

The authors declare that they have no conflict of interest

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