



## Status of adsorptive removal of dye from textile industry effluent

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### ABSTRACT

Textile industry is the key user of dyes and hence the prime source of water pollution, which risks aquatic as well as human life. There are various physical, chemical, and biological methods for dye removal, but most convincing is adsorption due to its simplicity. The extensive research has been carried out in this field which has brought a wide range of adsorbents in reach of industries. Freshly obtained off beat adsorbents in addition to direct one present have been used. The present paper aims at the broad classification of adsorbents recently introduced to the arena. The division of adsorbents comprises conventional means like activated carbon (commercial and derived), zeolite, and other nonconventional adsorbents as natural material, wastes, or even especially designed adsorbents, which are inexpensive and clean to use. Also, the investigations done regarding adsorption lately have been compared with respect to their results. The efficacy of each operation is under grave discussion. Up to 95% of the dye removal was observed in many cases with the adsorbent doses in the range of 1–20 g L<sup>-1</sup>.

*Keywords:* Textile industry effluent; Dye; Adsorption; Status; Review

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### 1. Introduction

Wastewater containing dyes as little as one ppm or even less [1] in its concentration holds the potential toxicological threat. Dyes are generally organic compounds. They are used for coloring textiles, paper, plastics, paints, and synthetic colorants. It is confirmed that nearly 40,000 dyes and pigments with variety of about 7,000 different chemical structures are present. Many of these are nonphotolytic, chemically resistant,

and nonbiodegradable in design [2]. In textile industry, about 10,000 dyes are being used for fiber dyeing and printing. During dyeing of textile, dye concentration may range from 10–200 mg L<sup>-1</sup>. Since the process of dyeing tends to lose 10–15% of dye to effluent [1,3], direct discharge of huge amount of industrial effluent in combination with increasingly stringent legislation makes the search for appropriate treatment technologies an important priority [4]. Application-based classification serves as basis for dye naming system color index (C.I.). The system comprises dye class, its hue, and a number (five digit C.I. number). For same C.I.

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number dye, chemical composition may vary for every manufacturer [5]. High toxicity and carcinogenicity of dyes is curse for textile industry, but its propagating rate of consumption is inevitable. The privileges which brought synthetic dyes to fame of industrial arena are vibrant colors, cheaper production, resistant to environmental factors, and comfortable usage. Any dye can be split into two parts i.e. chromophores and auxochromes. Chromophores are responsible for color, while auxochromes define the intensity for dye [6]. The huge runoff of dye effluent into water bodies is posing threat to human as well as marine life. It is a potent pollutant for wastewater treatment. The classification and applications of various dyes are given in Table 1 [7]. Dyes can be classified as acid, base, reactive, direct, disperse, solvent, sulfur, vat, etc. with wide applications and different application methods.

There are various physical, chemical, and biological methods for dye removal, but most convincing is adsorption due to its simplicity. The extensive research has been carried out in this field which has brought a wide range of adsorbents in reach of indus-

tries. Freshly obtained off beat adsorbents in addition to direct one present have been used. The present paper aims at the broad classification of adsorbents recently introduced to the arena. The division of adsorbents comprises conventional means like activated carbon (commercial and derived), zeolite, and other nonconventional adsorbents as natural material, wastes, or even especially designed adsorbents, which are inexpensive and clean to use. Authors group have widely worked on wastewater treatment and environmental engineering area [8–23].

## 2. Methods of dye removal

Industrial wastewaters may be treated in four stages: pretreatment, primary treatment, secondary treatment, and tertiary treatment. The initial preparatory phase for later phases is pretreatment comprising equalization and neutralization. In primary treatment pollutants are least handled, the suspended solids are subjected to physical or chemical removal techniques followed by secondary treatment which aims at

Table 1  
Type of dyes along with chemical, application, and application method [7]

Type	Chemical	Application area	Application method
Acid	Azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro, and nitroso	Nylon, wool, silk, paper, inks, and leather	Usually from neutral to acidic bath
Basic	Cyanine, hemicyanine, diazahemicyanine, diphenylmethane, triarylmethane, azo, azine, xanthene, acridine, oxazine, and anthraquinone	Paper, PAN, modified nylon, polyester, and inks	Applied from acidic dye baths
Reactive	Azo, anthraquinone, phthalocyanine, formazan, oxazine, and basic	Cotton, wool, silk, and nylon	Reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and pH (alkaline)
Direct	Azo, phthalocyanine, stilbene, and oxazine	Cotton, rayon, paper, leather, and nylon	Applied from neutral or slightly alkaline baths containing additional electrolyte
Disperse	Azo, anthraquinone, styryl, nitro, and benzodifuranone	Polyester, polyamide, acetate, acrylic, and plastics	Fine aqueous dispersions often applied by high temperature/pressure or lower temperature carrier methods; dye maybe padded on cloth and baked on or thermo fixed
Solvent	Azo, triphenylmethane, anthraquinone, and phthalocyanine	Plastics, gasoline, varnishes, lacquers, stains, inks, fats, oils, and waxes	Dissolution in the substrate
Sulfur	Indeterminate structures	Cotton and rayon	Aromatic substrate vatted with sodium sulfide and reoxidized to insoluble sulfur-containing products on fiber
Vat	Anthraquinone (including polycyclic quinines) and indigoids	Cotton, rayon, and wool	Water-insoluble dyes solubilized by reducing with sodium hydrogensulfite, then exhausted on fiber and reoxidized

biological removal. Finally, tertiary treatment is conducted to give up all pollutants out of water to reduce its potential toxicity for ecosystem as well as human. Coagulation/flocculation has found application as a process for dye removal from wastewater. The efficiency depends on the type of flocculant and on the pH of the medium [24]. Electrocoagulation was used for the effective removal of Acilan Blue from the wastewater of an operating textile plant in a bipolar packed-bed electrochemical reactor [25].

Membrane filtration can be used for improving the quality of potable as well as wastewater, using micro-filtration, ultrafiltration, nanofiltration, and reverse osmosis (RO). It is capable of extraction of chemicals from wastewater for reuse. Ultrafiltration and nanofiltration can be used for textile dye removal. The clogging of the pores of filter by dye molecules makes limited utility in industry. It is also uneconomical due to high working pressure, large energy consumption, costly membrane, and short life span of membrane. RO permeates only water, so, it is an efficient removal technique but is good for salt depletion than for weak

acid, weak base, and small molecules of organic nature. Hence, highly pure water can be produced [26–28].

Microbiological decomposition is a pretreatment process. It is very commonly used in dye effluent treatment. Many species of micro-organisms have already been used. It is widely used due to its economical aspect and the nontoxic product [5,29]. It can be a process in aerobic, anaerobic, and combined aerobic–anaerobic way.

Adsorption employing solid sorbents is widely used to remove certain classes of chemical pollutants from wastewater [30–39]. It is economical and has potential to treat commercial wastewater than any other method. The various dye removal methods along with their few advantages and disadvantages are outlined in Table 2.

### 3. Conventional means of adsorption

Activated carbon and zeolite are the main conventional adsorbents. These adsorbents are available at

Table 2  
Various physical, chemical, and biological methods for the removal of dye from wastewaters

	Method	Advantages	Disadvantages
Physical	Adsorption	Good removal of wide variety of dyes	Nonselective to adsorbate
	Membrane filtration	Remove all dye types	Concentrated sludge production
	Ion exchange	Regeneration: no adsorbent loss	Not effective for all dyes
	Irradiation	Effective oxidation at lab scale	Requires a lot of dissolved O <sub>2</sub>
	Electro kinetic coagulation	Economically feasible	High sludge production
	Coagulation–flocculation	Good elimination of insoluble dyes	Cost of sludge treatment garbage dump
	Adsorption on active carbon powder coupled with coagulation process	Matter, organic matter, and low influence on color Fast fouling of suspended matter	Cost of active carbon powder
Physical	RO	Retention of mineral salt and hydrolyzed reactive dyes and auxiliaries	High pressure process, Fouling with high concentrations
	Nanofiltration	Separation of mineral salts, hydrolyzed reactive dyes and auxiliaries	Treatment for complex solution with a high concentration of pollutant
	Ultrafiltration/microfiltration	Low pressure process	Inadequate quality for reused the permeate
Chemical	Fenton's reagent	Effective decolorisation of both soluble and insoluble dyes	Sludge generation
	Ozonation	Good elimination of color	No diminution of COD values Extra costs
	Photochemical NaOCl	No sludge production Initiates and accelerates azo-bond cleavage	Formation of by-product release of aromatic amine
	Electrochemical destruction	Breakdown compounds are	High cost of electricity
Biological	Standard Biological degradation	Efficiency of oxidizable matter 90%	Low biodegradability of dye, the salt concentration stay constant

ones ease, efficient in performance, fast enough in action, and having high surface area.

### 3.1. Activated carbon

Activated carbon is the more popular depleting agent for dye-based pollutants. Commercial activated carbon (CAC) has been proved its efficiency in industrial wastewater treatment. Economical aspects are the added advantage to use for dye removal [40]. Activated carbon is graphite with a random or amorphous structure, with high porosity, exhibiting a broad range of pore sizes, from visible cracks, crevices, and slits of molecular dimensions [41]. The adsorption capacity of the activated carbon is caused by surface reactivity, surface area, and a microporous structure [42]. Activation of carbon is done by cleaning up of less organized loosely bound carbonaceous material to clear the spaces between the elementary crystallites. The resulting channels through the graphitic regions, the spaces between the elementary crystallites, together with fissures within and parallel to the graphite planes constitute the porous structure, with a large internal surface area. Activation can be done either using physical/thermal or using chemical procedures. Activating physically or thermally substrate is carbonized at 500–600°C for volatile matter removal, later using CO<sub>2</sub>, steam, or fuel gas as mild oxidizing gas for partial gasification at 800–1,000°C to generate porosity and surface area either inculcates inorganic additives, metallic chlorides such as zinc chloride or phosphoric acid in substrate prior to carbonization to call it as chemical activation. ZnCl<sub>2</sub> activation produces activated carbons with a defined micro and mesoporous structure. For high surface area and pore volume, KOH activation is employed. The other chemicals used for activation are ammonium salts, borates, calcium oxide, ferric and ferrous compounds, manganese dioxide, nickel salts, hydrochloric acid, nitric acid, and sulfuric acid, etc. [42].

Powdered activated carbon (PAC) and granular activated carbon (GAC) are the two prime forms of activated carbon available in market. Precisely, for a continuous process GAC is more comfortable; hence, it is preferred for the study of removal of dyes from water. It need not be separated from fluid after use. But due to economic constraints and less contact time still PAC is being used [5,43]. The activated carbon can also be found in the forms of activated carbon pellet and activated carbon fiber (ACF). Pellets of activated carbon are generally physically activated from pulverized coal which is reagglomerated with suitable binder. For ACF, the carbon fibers are generally prepared from polymeric precursor materials such as polyacrylonitrile

(PAN), cellulose, pitch, and polyvinylchloride; of these, PAN-based carbon fibers predominate and have good strength and modulus properties, whereas carbon fiber can be made with a higher modulus, albeit a lower strength, using a pitch-based precursor. These carbon fibers after activation using same methodology result in high surface area carbon [5].

#### 3.1.1. Commercial activated carbon

The CAC has a sufficiently high efficiency for the pollutant removal. Hence, despite its cost and nonselectivity to substrate, it is a popular adsorbent. Batch adsorption and desorption of Naphthol Yellow S were studied for different ranges of adsorbent used, contact time, concentration, temperature, and pH [44]. Dye removal rate increases from 0.1 to 0.5 g L<sup>-1</sup> and gradually starts reducing. The adsorption reduces with increase in initial concentration of dye, while actual dye adsorbed per unit mass of adsorbent increase with increase in dye concentration. The equilibrium was attained in 20 min. With increase in dye concentration, removal of dye reduces from 94.41 to 82.60% for activated carbon. Activated carbon is hardly affected by pH of solution for adsorption of Naphthol Yellow S dye. For different particle sizes, maximum adsorption was obtained at <106 BSS (British standard size) mesh size, i.e. 90%. Dye adsorption was elevated with increase in speed of agitation from 50 to 250 rpm. The process of adsorption of Naphthol Yellow S was endothermic and its adsorption increases in order 30 < 40 < 50°C. Also, the chemical oxygen demand (COD) reduces from 1,860 to 186 mg L<sup>-1</sup> [44].

Adsorption efficiency of activated carbon (Norit RB 0.8CC) for removal of chromium complex dye LanasyN Navy M-DNL from aqueous solution was studied [45]. Investigation involved experiments for different conditions of initial dye concentration, pH, and temperature. The efficiency of removal was measured in terms of residual color to show dependency on initial concentration of the dye. This efficiency was increased at lower concentrations, whereas it was decreased at higher concentrations. Two theoretical models (pseudo-second-order-reaction and intraparticle diffusion) were used to describe the sorption kinetics and to determine the constants of sorption rate ( $k_2$ ), intraparticle ( $k_i$ ), and film diffusion ( $k_s$ ) [46]. Microporous GAC type F400 was used for the adsorption of three acid dyes, such as Acid Black 80 (AB80), Acid Red 114 (AR114), and Acid Yellow 117 (AY117), from aqueous solution in a batch system [47]. In order to determine the best fit isotherm for each system chi-square ( $\chi^2$ ), log-likelihood ( $G^2$ ), residual root mean square error (RMSE), sum of the squares of the errors

(ERRSQ), composite functional error (HYBRD), derivative of Marquardt's percent standard deviation (MPSD), average relative error (ARE), sum of absolute error (EABS), and average percentage error (APE) analysis methods are applied [47]. The Langmuir, Freundlich, Dubinin–Radushkevich, Temkin, Halsey, Jovanovic, and Harkins–Jura models were compared [47]. It was concluded that lower capacity systems using molecular weight dyes on the microporous carbon favor the Temkin isotherm. The smaller molecular mass dye adsorbing onto the microporous carbon is represented equally by the Langmuir and the Temkin isotherm models [47].

The CAC, Chemviron GW was used to adsorb Acid Blue 113 (AB 113) to compare the results with activated carbon derived from waste tire rubber [48]. The dye adsorption increased as dose of adsorbent increases from 1 to 5 g L<sup>-1</sup>, which decreases as the dose is increased from 5 to 20 g L<sup>-1</sup>. Increased adsorbent dose shows less commensurate increase in adsorption resulting from lower adsorptive capacity utilization of adsorbent [49]. Optimum pH was found to be 5. The amount adsorbed increase with decreasing particle size and surface area. Acid Blue 113 attained equilibrium in 60 min. It was observed that adsorption decreased with increase in temperature [48].

### 3.1.2. Activated carbon synthesized from waste

Various waste materials specifically agriculture waste can be converted into activated carbon which can help to reduce the cost of waste disposal and provide a potentially inexpensive alternative to the CAC. Adsorption of Lanaset Grey G, an industrial metal complex dye on activated carbon derived from Tunisian olive-waste cakes, was studied [50]. The adsorption capacity of the adsorbent was found to be 108.7 mg g<sup>-1</sup> which is far better than that of a CAC. The activated carbon was prepared by chemical activation of exhausted olive-waste cakes. Acid concentration and impregnation ratio are important factors that govern the development of porosity of the prepared carbon [51]. Also, the adsorption of dyes of different chemical structures and the effect of pH on the solute uptake by activated carbons can be high, moderate, or slightly significant were studied [5,52–54]. The contact time needed to reach adsorption equilibrium of Lanaset Grey G on activated carbon is about 50 h for all the adsorbent loadings [50]. For equilibrium attainment, 48 h as a contact time was used to adsorb Acid Green 25 dye [55]. The process of adsorption of Lanaset Grey G on olive-waste cake derived carbon is endothermic [50]. The Langmuir isothermal model provides the best fit of the experimental data. The

application of the intraparticle diffusion model revealed that the adsorption mechanism of this dye is rather a complex process and the intraparticle diffusion is involved in the overall rate of the adsorption process, but it is not the only rate-controlling step [50].

Residual errors analysis was conducted for adsorption of two acid dyes, Acid Black 1 (AB1) and Acid Blue 113 (AB113), on mesoporous granular pine-cone derived activated carbon (GPAC) in batch system [47]. GPAC was produced by exposing the raw pine-cones to a thermal–chemical process [56]. A mesoporous activated carbon derived from waste tire rubber was used to adsorb Acid Blue 113 (AB113) and the results were compared with CAC [48]. The ground tire granules were thermo-chemically treated to bring out the desired activated carbon. The dye adsorbed was found to be rapid from 1 to 10 g L<sup>-1</sup>, which then slowed down as the dose increased from 10 to 20 g L<sup>-1</sup>. Change in initial dye concentration rendered amount of dye adsorbed per unit mass of adsorbent increase from 0.84 to 9.72 mg g<sup>-1</sup>. This suits the finding which has been quoted by the other researchers [57,58].

The activated carbon derived from the pods of *Thespesia populnea* was used for adsorption of Orange G dye from aqueous system [59]. *Thespesia populnea* is a large tree found in the tropical regions and coastal forests of India. The pods were chemically carbonized. It was observed for adsorption of 17.6 mg L<sup>-1</sup> of Orange G dye a maximum 0.54 g of activated carbon is required. Equilibrium was established in time period of 4.03 h. The effects of various parameters, such as agitation time, initial dye concentration and adsorbent dosage, were studied using response surface methodology (RSM) [59]. The potential use of activated carbon prepared from the epicarp of *Ricinus communis* for the removal of Malachite Green (MG) dye has been proved [60]. The epicarp of *Ricinus* is a segregated waste by-product (35% of production) during segregation of *R. communis* seed. The epicarp of *Ricinus* was previously investigated to adsorb crystal violet and Ni (II) [61,62]. The epicarp was chemically charred using acid and then crushed to granules. Adsorption was found to be lowest at pH 2.0 and highest at pH ~7.0. The trend of pH effect observed was similar to the adsorption of MG on activated carbon prepared from fly ash and tuncbilek lignite [63,64]. The equilibrium was attained in 90 min [60]. The adsorption was increased from 4.17 to 20.18 mg g<sup>-1</sup> as the dye concentration increased from 25 to 200 mg L<sup>-1</sup>. The adsorption increased from 48.65 to 76.92 %, as the adsorbent dose increased from 0.2 to 1.0 g 50 mL<sup>-1</sup> at equilibrium. The adsorption kinetics follows the pseudo-second-order rate with

intraparticle diffusion as one of the rate determining steps [60].

Activated carbon derived from Brazilian pine-fruit shells (*Araucaria angustifolia*) was used for removal of Remazol Black B (RB) textile dye from aqueous effluents [65]. It was proposed, the use of Brazilian pine fruit shell as precursor for the preparation of the activated carbon material [66]. It is a material having high surface area (subdivided pieces of carbon) that could lead to an increase in the maximum amount adsorbed of the RB dye [65]. The maximum adsorption capacity for derived activated carbon is  $446.2 \text{ mg g}^{-1}$ . RB uptake was favorable at pH values ranging from 2.0 to 7.0. The contact time required to obtain the equilibrium using the activated carbon was 4 h at 298 K. The results with derived activated carbon were better than pure biosorbent [65]. Activated carbon derived from *Borassus aethiopicum* flower was used for the removal of MG from aqueous solutions by varying pH, adsorbent dosage, initial dye concentration, and temperature with three different particle sizes, such as 100, 600, and  $1,000 \mu\text{m}$  [67]. Palm is the common name for *Borassus aethiopicum*. Palm flower was collected from Pondicherry, India. Activated carbon was prepared from the biomass. The adsorbent surface area was found to be  $9.57 \text{ m}^2 \text{ g}^{-1}$  and total pore volume is  $0.0737 \text{ cm}^3 \text{ g}^{-1}$ . Maximum adsorption occurred at pH ranging from 6.0 to 8.0. When adsorbent dosage was increased from 0.001 to  $0.5 \text{ g}/10 \text{ mL}$ , it was observed that, for 100, 600, and  $1,000 \mu\text{m}$ , the percentage adsorption varied from 83 to 99, 33 to 99, and 31 to 98, respectively. But the percentage adsorption decreased after  $0.1 \text{ g}$  [67], it may be due to the decrease in total adsorption surface area available to MG resulting from overlapping or aggregation of adsorption sites [68].

The adsorption on activated carbon followed pretreatment using coagulation/flocculation for Reactive Black 5 dyes and Reactive Orange 16 dyes was studied [69]. Activated carbon derived from coconut shells was used as the adsorbent and aluminum chloride was used as the coagulant. The maximum adsorption capacity increases from  $16.6$  to  $19 \text{ mg g}^{-1}$  with a pH increase from 2 to 3, while it decreases to  $5.8 \text{ mg g}^{-1}$  with an increase to pH 7. It can be concluded that pH 3 is the optimum value for the color removal process. It was found that the time required for the solutions with added salt to reach equilibrium was approximately 5 h 40 min; in the case of the solution without sodium chloride the adsorption was slow, with equilibrium being reached in 6 h 20 min, for both dyes. The presence of salt positively influences the adsorption when compared with the experiments in its absence [70]. The adsorption potential of bamboo

waste-based granular activated carbon (BGAC) to remove C.I. Reactive Black (RB5) from aqueous solution was investigated using fixed-bed adsorption column [71]. Bamboo waste used for preparation of GAC was obtained from local furniture factory in Malaysia. The chemical activation method was used. The highest bed capacity found was  $39.02 \text{ mg g}^{-1}$  using  $100 \text{ mg L}^{-1}$  inlet dye concentration, 80 mm bed height, and  $10 \text{ mL min}^{-1}$  flow rate. With the increases in influent concentration, RB5 loading rate increases, so, does the driving force increase for mass transfer, which renders a decrease in the adsorption zone length [72]. Trends were similar for adsorption of methylene blue (MB) by rice husk [73] and removal of acid dye using pristine and acid-activated clays [74]. High adsorption capacity was observed at the highest bed height due to an increase in the surface area of adsorbent [75,76].

### 3.2. Zeolite

Zeolites have high selectivity as an adsorbent, high ion-exchange caliber, and high surface areas. It is the most prevalent form of microporous crystalline alumina-silicates. It occurs naturally as well as processed for use. Most studied zeolite form is clinoptilolite, it has a characteristic of tabular structure [77]. Zeolites pose a problem due to its low permeability and inoperability in column without support. It was found that clinoptilolite is an inefficient adsorbent for reactive dyes [78–81]. This inefficiency shall be credited to the intricate mechanism of adsorption for its porosity, charging at different levels of surface, heterogeneity, and imperfections present over the surface.

The adsorption of Reactive Blue 21 (RB21) and Reactive Red 195 (RR195) and their different combinations on clinoptilolite was investigated [82]. The clinoptilolite was obtained from the rhyolitic tuff level of the Neogene volcano sedimentary sequence in Gordes, West Anatolia, Turkey. Two mono-component (RB21 and RR195) and binary component (RB21 with RR195 and RR195 with RB21) isotherms were determined. The mono-component Langmuir isotherm model was applied to experimental data and the isotherm constants were calculated for RB21 and RR195 dyes [82].

## 4. Nonconventional means of adsorption

The nonconventional adsorbents may be classified into two ways either on the basis of their availability: natural materials, industrial/agricultural/ domestic wastes or by-products, and synthesized products or depending on their nature: inorganic and organic [5].

#### 4.1. Natural materials

##### 4.1.1. Chitin and chitosan

Chitin is a polysaccharide found ample in nature. The exoskeleton of crustaceans is known to contain chitin [83]. Chitosan is derivative of chitin, produced by deacetylation to form a type of polyaminosaccharide. Chitosan's vulnerable nature to pH does not let it stand variation in pH values [84,85]. Cross-linking is used for enhancement of the adsorptive properties of chitosan by making it withstand the acidity of solution along with improvement in toughness of adsorbent [1,84,86]. A composite of chitosan/montmorillonite for adsorption of Congo Red (CR) with adsorption capacity  $53.42 \text{ mg g}^{-1}$  to work at  $30^\circ\text{C}$ , follows pseudo-second-order model and Langmuir isotherm, was investigated and discovered [87]. Similarly, chitosan/activated clay composite was used for the adsorption of MB and Reactive red 222 (RR 222) [88]. The adsorption capacities are  $330 \text{ mg g}^{-1}$  and  $1921 \text{ mg g}^{-1}$  for MB and RR 222, respectively, at temperature  $30^\circ\text{C}$ , following Freundlich isotherm. MB showed maximum adsorption at pH 7.1, whereas RR 222 at 6.5 [88].

Direct Blue 78 (DB78) and Acid Black 26 (AB26) adsorption on biocompatible composite (chitosan–zinc oxide nanoparticle, CS/n-ZnO) was investigated. Zinc oxide nanoparticles can be immobilized onto chitosan [89]. The effect of CS/n-ZnO doses, initial dye concentration, salt, and pH was noted at  $20 \pm 1^\circ\text{C}$ . Due to the advantages of being nontoxic, antibacterial, and biodegradable, chitosan and its derivatives have been attracting more and more attention [90]. The different chitosan composites, such as chitosan/ $\text{TiO}_2$ , chitosan/activated clay, and chitosan/CdS were prepared and used for adsorption [85,91–93]. Chitosan extracted from snow crab shell with degree of deacetylation 98.5% and average molecular weight of 200 KD was used [89]. Maximum adsorption occurred at pH 2. It was found that AB26 and DB78 followed Langmuir and Tempkin isotherms, respectively. The adsorption kinetics for both dyes was found to be pseudo-second-order kinetics [89].

The effect of chitosan beads in adsorption of effluent generated at the waste stream end of cotton textile dyeing process was studied [94]. Industrial effluents from the dyeing reactor of a dyeing firm of Greece and composed of three reactive dyes, Remazol Red 3BS (RR), Remazol Blue RN (RB), and Remazol Yellow Gelb 3RS (RY), were used. The composition of each dye were found to be  $197 \text{ mg L}^{-1}$  RR,  $223 \text{ mg L}^{-1}$  RY, and  $280 \text{ mg L}^{-1}$  RB in the effluent. Cross-linked chitosan beads of grafted (addition of amido and imino groups on chitosan backbone through grafting reactions) and of nongrafted nature are used for study. Three types of

cross-linked chitosan adsorbents were synthesized: (i) nongrafted chitosan beads (Ch) [95], which were used as reference in all experiments, (ii) chitosan beads grafted with acrylamide (Ch-g-Aam) [95,96], and (iii) chitosan beads grafted with poly(ethylene imine) (Ch-g-PEI) [97–99]. Grafting increase the adsorption capacity, whereas cross-linkage developed beads to stand 10 cycles of adsorption–desorption without any significant loss in adsorption capacity [94].

##### 4.1.2. *Eucalyptus camaldulensis* Bark

Tree barks (*Eucalyptus camaldulensis* was found from wet tropic to cold temperate zone and can withstand arid condition) were used for the adsorption of textile dyes (Basic Blue 41—BB41 and Reactive Black 5—RB5) [100]. There is slight work on the study of dye adsorption tendency of *Eucalyptus* tree barks [101]. In the south region of Turkey, *E. camaldulensis* is a common species [100]. It is large evergreen tree variety native to Australia. The barks of *E. camaldulensis* were collected from Balcal campus of the University of Cukurova (Adana, Turkey). The collected barks were washed with hot distilled water ( $60 \pm 2^\circ\text{C}$ ) and dried at room temperature before being crushed. It can be seen that the rise in the inlet dye concentration reduces the volume treated before the *E. camaldulensis* barks get saturated. A high dye concentration may saturate the *E. camaldulensis* barks more quickly, thereby decreasing the breakthrough time. This was a common observation that the higher influent concentration and the lower bed depth could result in poor effluent quality. The Bohart–Adam's equation's linear plots were used to determine characteristic parameter for each dye and related correlation coefficients [100].

##### 4.1.3. Pillared Interlayered clays

Pillared interlayered clays (PILCs) are chemically altered form of clay that is created by the intercalation of soils [102]. The dyes Orange II and MB have served as model dyes for the experimental observation. The detailed preparation, textural characterization, and catalytic properties at different conditions were studied [103–105]. The clay was intercalated with aluminum and zirconium hydroxy-polycations following a predetermined practice [106,107]. Al-PILC and Zr-PILC are the resulting solids [102]. This has been estimated that stirring for 300 min could easily bring the dye/pillared clay system to equilibrium. The pillared clays have the same adsorption capacity for Orange II, whereas the adsorption capacity of Zr-PILC for MB is higher than that for Al-PILC. This may be supposed to favor the result that dye adsorption is

not sensitive to the same type of porosity. The addition of NaCl has been found to increase the adsorption capacities of the two pillared clays for Orange II [102].

#### 4.1.4. Humin

Humin was used for adsorption/desorption of reactive dyes in both batch experiments and fixed bed columns, when humin is immobilized on silica, the optimum conditions were determined [108]. Peat is an organic soil formed during a complex process of decomposition and humification of plant residues by microbiological oxidation in flooded environments [109,110]. Both humin and peat have been proved as valuable materials for removal of dyes [111]. The depth of 0–60 cm in the Santo Amaro das Brotas peatland, Sergipe State, Brazil was used for peat sample collection, later it was air dried, homogenized, ground in a porcelain mortar, and sieved through a nine-mesh screen [111]. The extraction of Humin followed the procedure for extraction of soil humic substances [112]. For batch studies, it can be seen that adsorption equilibrium was achieved rapidly for all of the initial concentrations, in 30–45 min Reactive Red (RR) 120 and Reactive Orange 16 [108]. Results show that adsorption of Reactive Orange 16 and RR 120 by humin was most effective at pH 1.0. It can be seen that the adsorption capacity of the adsorbents decreased with increasing temperature, indicative of an exothermic process. It is also possible that a very high temperature could favor the desorption process, in the case of exothermic adsorption [113]. For the column studies, procedure adopted for immobilization of the humin biomass was similar to that reported in [114]. The dyes were completely retained on the column in the first adsorption cycle, for the first 75 and 175 min, considering the case of Reactive Orange 16 and RR 120, respectively [108].

## 4.2. Waste and products from Industrial/agricultural/domestic field

### 4.2.1. Deoiled mustard (ADM)

The ADM has been used to adsorb Erythrosine dye efficiently [115]. Batch study of Naphthol Yellow S removal using de-oiled mustard was carried out [44]. The rate of dye removal vary for different ranges of ADM loading, it increases with increase from 1 to 4 g L<sup>-1</sup> and remains constant for increase from 4 to 6 g L<sup>-1</sup>. The adsorption reduces with increase in initial concentration of dye, while actual dye adsorbed per unit mass of adsorbent increase with increase in dye concentration. The equilibrium is attained in 80 min.

With increase in dye concentration, percentage removal of dye reduces from 81.40 to 65.80% for ADM. The pH of the aqueous solution is an important controlling parameter in the adsorption process [116]. Adsorption is influenced by pH of solution and zero point charge of adsorbent [44].

### 4.2.2. Brazilian pine-fruit shells

The investigations to estimate the adsorption tendency of Brazilian pine-fruit shells (*Araucaria angustifolia*) for removal of RB textile dye from aqueous effluents have been conducted [65]. The Brazilian pine-fruit shell was dried and milled to serve as biosorbent [117,118]. It is a compact fibrous material presenting some fissures and macropores. The maximum adsorption capacity for biosorbent is 74.6 mg g<sup>-1</sup>. RB uptake was favorable at pH values ranging from 2.0 to 2.5. The contact time required to obtain the equilibrium was 12 h at 298 K [65].

### 4.2.3. Bamboo char

Bamboo char was prepared from the scaffolding of waste bamboo for Acid Blue 25, Acid Yellow 117, and MB dye removal from wastewater [119]. Bamboo char with a surface area up to 563.6 m<sup>2</sup> g<sup>-1</sup> was prepared with yield of char of about 25.8% [120]. Raw bamboo was obtained from a construction site in the campus of Hong Kong University of Science and Technology [119]. When the raw material was heated to 900 °C for 2 h, surface area and total pore volume were 327 m<sup>2</sup> g<sup>-1</sup> and 0.185 cm<sup>3</sup> g<sup>-1</sup>, respectively. Particle size and heating rate appear less influential to the yield and textural characteristics of the resultant chars. The Bamboo char did not show very high adsorption capacities for two acid dyes (Acid Blue 25 and Acid Yellow 117) but exhibited significant uptake of MB [119].

### 4.2.4. Cashew nut shell (CNS)

The low-cost adsorbent was prepared from the CNS agricultural waste [121]. It has been utilized as the adsorbent for the removal of CR dye from an aqueous solution. The effect of pH, adsorbent dose, initial dye concentration, time, and temperature on adsorption was studied. CNS were collected from Pudukkottai District, Tamilnadu, India. This natural waste was crushed into powder and sieved through the sieves of 200–30 mesh size particles. The pH of the system exerts profound influence on the uptake of CR molecule presumably due to the effect it poses on the surface properties of the adsorbent. It has been shown



that the maximum removal of dye is at pH 3 and below. The percentage removal increases from 56.33 to 99.34% for an increase in adsorbent dose from 5 to 30 g L<sup>-1</sup> of the adsorbent. By increasing adsorbent dose, the amount of dye adsorbed onto unit weight of CNS gets reduced, thus causing a decreasing in adsorption capacity value with increasing CNS dose. While the percentage dye removal was found to be 98.52% for 20 mg/L of initial concentration, this value was 85.44% for that of 100 mg L<sup>-1</sup>. The adsorption of dye on CNS was investigated as a function of temperature and maximum removal of CR was obtained at 30°C. Due to the effect of contact time, the percentage removal increases with time up to 90 min and remains almost constant. Thermodynamically, it has been proven that the sorption process was feasible, spontaneous, and exothermic in nature. It was shown that the adsorption of CR could be described by the pseudo-second-order equation, suggesting that the adsorption process presumably is chemisorptions [121].

#### 4.2.5. Pistachio hull powder (PHP)

The pistachio hull an agricultural waste was used to prepare an adsorbent for the certain cationic dyes. Removal of MB as a cationic model dye by PHP from aqueous solution was studied. Pistachio hulls are a waste generated in pistachio peeling factories and are accessible in bulk at no cost [122,123]. Its efficacy has been observed at pH (2–10), PHP dosage (0.5–3 g L<sup>-1</sup>), MB concentrations (100–400 mg L<sup>-1</sup>), contact time (1–70), and solution temperature (20–50°C). MB adsorption onto PHP increased from 59.2% to a maximum of 99.6%, when the rise in solution pH was from 2 to 8. A similar trend was also reported for MB adsorption from aqueous solution as a function of pH by other researchers, including yellow passion fruit peels [124], papaya seeds [125], and jackfruit peel [126]. The best results are at pH 8 for maximum MB removal in solution [122]. The degree of removal attained a maximum of 92 and 97.5% at 70 min for doses of 0.5 and 1 g L<sup>-1</sup>, respectively, while 99.7 and 99.9% MB removal efficiencies were achieved for 70 min contact time in the presence of 1.5 and 2 g L<sup>-1</sup> PHP, respectively. The enhancement of MB removal as a function of PHP dose is due to the presence of a greater surface for adsorption and thus, more available sites [126].

#### 4.2.6. Modified sugarcane bagasse lignin

The lignin residual left after acid hydrolysis of sugarcane bagasse during bioethanol production from

biomass was purified and substituted with carboxymethylated to obtain a macromolecule (CML), soluble in water at pH  $\geq 4.5$ , with a degree of substitution of  $0.46 \pm 0.01$  relative to C9—the basic unit of lignin [127]. To use it as efficient adsorbent for Brilliant Red 2BE textile dye from aqueous solutions, modified lignin was complexed with the Fe<sup>3+</sup> ion to form CML-Fe. Originally found lignin or chemically modified lignin is always a cheap and environment friendly alternative for entrapping pollutants from water [128–131]. Isolated lignin after saccharification employed in adsorbent formation was obtained from Company Dedini SA, São Paulo, Brazil [127]. The superficial area of the CML-Fe adsorbent was compatible with modified biosorbent containing metallic ion, which favored the adsorption of an anionic dye. The maximum adsorption of the dye was attained at pH 2.0 [132]. Increases in the percentage of the dye removal were up to adsorbent mass of 50 mg, this could be attributed to increases in the adsorbent surface areas, augmenting the number of adsorption sites available for adsorption, and it has already been reported in several papers [66,133–137].

#### 4.3. Synthetic materials

A neutral polymeric adsorbent macronet MN 200 was used for the removal of chromium complex dye Lanasyne Navy M-DNL [45]. It has been investigated under various experimental conditions of initial dye concentration, pH, and temperature. The dye removal efficiency was characterized by the values of the residual color, which depended on initial concentration of the dye. This efficiency increased at lower concentrations, while it decreased at higher concentrations. Here, the comparison of macronet MN 200 is with those treated using activated carbon. But the maximum removal of chromium ions using macronet MN 200 was obtained when the initial concentration of chromium complex dye ranged from 4 to 50  $\mu\text{mol/L}$ , while maximum removal of organics when the initial concentration was lower than 100  $\mu\text{mol/L}$  [46]. The removal of dye is more effective in acidic media (pH  $\leq 2$ ) as compared to that at pH  $\geq 7$ . Whereas under identical conditions, dye removal using macronet MN 200 is more effective than that using activated carbon. The residual color for macronet MN 200 at pH  $\leq 2$  and initial concentration increasing from 4 to 100  $\mu\text{mol/L}$  was below 10%. In the first 30 min, 98% of the dye adsorption by MN 200 occurred at pH 2 and temperature of 20°C, whereas 88% of the adsorption at pH 7 and the same temperature [45].

Table 3  
Summary of few studies on adsorption of various dyes by prepared or CAC

Adsorbent	Adsorbate	Adsorption capacity ( $\text{mg g}^{-1}$ )	pH	Temp ( $^{\circ}\text{C}$ )	Kinetic model	Isotherm	Reference
Activated carbon commercial	Naphthol Yellow S	–	2.5	50	Pseudo-first order	Freundlich & Langmuir	[44]
Activated carbon Norit RB 0.8	Anionic Lanasyn Navy M-DNL (chromium complex)	–	2–7	20, 40	Pseudo-second order	–	[45]
GAC from Pine cone	Acid Black 1	452.9	7.5±0.2	20	–	Langmuir	[47]
	Acid Blue 113	298.4	7.5±0.2	20	–	Langmuir	[47]
GAC type F400	Acid Black 80	171.5	–	20	–	Langmuir	[47]
	Acid Red 114	103.7	–	20	–	Tempkin	
	Acid Yellow 117	185.8	–	20	–	Tempkin	
Activated Carbon from Rubber tire	Acid Blue 113	–	2	–	Pseudo-first order	Langmuir	[48]
Activated Carbon Commercial	Acid Blue 113	–	5	–	Pseudo-first order	Langmuir	[48]
Activated Carbon from Tunisian olive waste Cake	Lanaset Grey G (Metal complex)	108.7	6	25	Pseudo-first order	Langmuir	[50]
Activated Carbon from Thespesia populnea pod	Orange G	–	–	–	Pseudo-second order	Langmuir & Freundlich	[59]
Activated Carbon from Epicarp of Ricinus Communis	MG	–	7	27 ± 2	Pseudo-second order	Langmuir	[60]
Activated Carbon from Brazilian Pine fruit shells (Araucaria Angustifolia)	RB	446.2	2–7	25	Fractionary order model	Sip's isothermal model	[65]
Activated carbon from Borassus Aethiopicum flower (palm)	MG	–	6–8	40	Pseudo-second order	Langmuir	[67]
Activated carbon from coconut shell	Reactive Black 5	–	3	70	–	Langmuir, Freundlich & Radhke-Prausnitz	[69]
	Reactive Orange 16	–	3	70	–	–	
GAC from Bamboo waste	Reactive Black 5	39.02	6.5	28	Second order	Thomas Yoon-Nelson	[71]
CAC Norit-SAE-2	Industrial reactive dye effluent from Greek industry. Contains Remazol Red 3BS, Remazol Blue RN, Remazol Yellow Gelb 3RS	521	2	25	–	Langmuir & Freundlich	[94]

Clinoptilolite (Zeolite)	Reactive Blue 21	9.652	–	25	Pseudo-second order	Langmuir	[138]
	RR 195	3.186	–	25	Pseudo-second order	Langmuir	
Activated carbon from sugarcane bagasse pith	Reactive Orange	–	–	–	Pseudo-second order	Langmuir & Freundlich	[139]
Activated carbon from aqueous solution Pomegranate peel	Direct Blue 106	–	2	–	Pseudo-second order	–	[140]
Activated carbon	Acid Red 97	–	–	–	Pseudo-second order	Freundlich	[141]
	Acid Orange 61	–	–	–	Pseudo-second order	Freundlich	
	Acid Brown 425	–	–	–	Pseudo-second order	Freundlich	
Activated carbon commercial grade	MG	–	7	–	Pseudo-second order	Freundlich	[142]
Activated carbon laboratory grade	MG	–	7	–	Pseudo-second order	Redlich-Peterson	
Activated carbon from Rice husk	Acid Blue (CI 73015)	50	–	25	First order	Langmuir	[143]
	Acid Yellow (CI 19140)	50	–	25	First order	Langmuir	
Filtrisorb 400 (Calgon corporation)	Direct Brown 1 (CI 30110)	7.69	–	–	First order (reversible)	Langmuir	[144]

Table 4  
Summary of few studies on adsorption of various dyes by low-cost adsorbent prepared from various wastes

Adsorbent	Adsorbate	Adsorption capacity (mg g <sup>-1</sup> )	pH	Temp (°C)	Kinetic model	Isotherm	Reference
MgO Nanoparticles	Reactive Blue 19	166.7	8	–	Pseudo-second order	Langmuir	[6]
	RR 198	123.5	8	–	Pseudo-second order	Langmuir	
De-oiled mustard	Naphthol Yellow S	–	2.5	30	Pseudo-first order	Freundlich & Langmuir	[44]
Macronet MN 200	Anionic Lanasyne Navy M-DNL (chromium complex)	–	2–7	20, 40	Pseudo-second order	–	[45]
Brazilian Pine fruit shells (Araucaria Angustifolia)	RB	74.6	2–2.5	25	Fractionary order model	Sip's isothermal model	[65]
Peanut husk	MB	–	–	–	Pseudo-second order	Tempkin	[73]
Chitosan-Zinc oxide nanoparticle	Direct Blue 78	100	2	20	Pseudo-second order	Tempkin	[89]
	Acid Black 26	100	2	20	Pseudo-Second order	Langmuir	
Chitosan bead (Ch)	Industrial reactive dye	447	2	25	–	Langmuir & Freundlich	[94]
Chitosan bead grafted with acrylamide (Ch-g-Aam)	effluent from Greek industry. Contains Remazol	1,052	2	25	–	Langmuir & Freundlich	
Chitosan bead grafted with poly(ethyleneimine) (Ch-g-PEI)	Red 3BS, Remazol Blue RN, Remazol Yellow Gelb 3RS	1,352	2	25	–	Langmuir & Freundlich	
Zirconium pillared clay (Zr-PILC, chemically modified)	Orange 2	–	7	25	Pseudo-second order	Sip's isothermal model	[102]
	MB	–	7	25	Pseudo-second order	Sip's isothermal model	
Aluminum pillared clay (Al-PILC, chemically modified)	Orange 2	–	7	25	Pseudo-second order	Sip's isothermal model	[102]
	MB	–	7	25	Pseudo second order	Sip's isothermal model	
Humins	Reactive Orange 16	–	1	25–45	Pseudo-second order	Freundlich	[108]
	RR 120	–	1	25–45	Pseudo-second order	Langmuir	
Char from Bamboo	MB	316.65	–	–	–	Redlich-Peterson	[119]
	Acid Blue 25	–	–	–	–	Redlich-Peterson	
	Acid Yellow 17	–	–	–	–	Redlich-Peterson	
CNS	CR	–	≥3	30	Pseudo-second order	Redlich-Peterson	[121]
Pistachio hull waste	MB	389–602	8	20–50	Pseudo-first order	Langmuir	[122]
Modified Sugarcane Baggasse lignin	Brilliant Red 2BE	6.5–15.1	2	25	Avrami fractional order	Sip's isothermal model	[127]
Bagasse fly ash	MG	–	7	–	Pseudo-second order	Freundlich	[142]

Charfines	Direct Brown 1 (CI 30110)	6.4	–	–	–	–	–	–	First order (irreversible)	Rearranged Langmuir	[144]
Lignite coal	Direct Brown 1 (CI 30110)	4.1	–	–	–	–	–	–	First order (irreversible)	Rearranged Langmuir	
Bituminous coal	Direct Brown 1 (CI 30110)	2.04	–	–	–	–	–	–	First order (irreversible)	Rearranged Langmuir	[145]
Fe <sub>3</sub> O <sub>4</sub> Hollow nanosphere	Neutral Red	105	6	–	–	–	25	–	Pseudo-second order	Langmuir	[146]
Nano-cellulose hybrid containing Polyhedral Oligomeric Silsesquioxane	Reactive Yellow B-4RFN	–	–	–	–	–	–	–	Second order	–	
TiO <sub>2</sub> suspension	Reactive Blue B-RN	–	–	–	–	–	–	–	Second order	–	
	Procion Yellow H-EXL	–	5	–	–	–	–	–	Pseudo-first order	Langmuir Hinshelwood's heterogeneous catalytic model	[147]
Chitosan Nano particle	Acid Orange 10	1.77	2	–	–	–	25 ± 1	–	–	Langmuir	[148]
	Acid Orange 12	4.33	2	–	–	–	25 ± 1	–	–	Langmuir	
	Acid Red 18	1.37	2	–	–	–	25 ± 1	–	–	Langmuir	
	Acid Red 73	2.13	2	–	–	–	25 ± 1	–	–	Langmuir	
Polymeric Gel	Bromo-phenol Blue	–	–	–	–	–	–	–	Pseudo	–	[149]
	MB	–	–	–	–	–	–	–	Pseudo	–	
	MG	–	–	–	–	–	–	–	Pseudo	–	
Chitosan Nano particle	RR 120	–	4.5	–	–	–	25	–	Pseudo-second order	–	[150]
Rejected Tea	MB	147	–	–	–	–	30	–	Pseudo-second order	Langmuir	[151]
Chitosan/kaolin/ $\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	Methyl Orange	–	6	–	–	–	–	–	–	–	[152]
Neem sawdust	MG	4.354	–	–	–	–	–	–	–	Langmuir	[153]
Modified basic oxygen furnace slag	Reactive Black 5	76	2	–	–	–	–	–	First order	Langmuir & Redlich-Peterson	[154]
	Reactive Blue 19	60	2	–	–	–	–	–	First order	Langmuir & Redlich-Peterson	
Chemically treated Wood shavings	RR 120	55	2	–	–	–	–	–	First order	Langmuir & Redlich-Peterson	[155]
	MB (basic dye)	–	–	–	–	–	–	–	–	Langmuir & Freundlich	
Silica Nano-sheets derived from Vermiculite	Egacid orange (acid dye) MB	–	–	–	–	–	–	–	–	Langmuir & Freundlich	
Chitosan	Basic Blue 3	–	–	–	–	–	20	–	Pseudo-second order	Langmuir	[156]
Modified Chitosan	Basic Blue 3	–	–	–	–	–	–	–	–	Langmuir	[157]
Cyclodextrin polymer	Basic Violet 3	53.2	–	–	–	–	–	–	Pseudo-second order	Freundlich	[158]
	Basic Blue 3	42.8	–	–	–	–	–	–	Pseudo-second order	Freundlich	
	Basic Violet 10	35.8	–	–	–	–	–	–	Pseudo-second order	Freundlich	

(Continued)

Table 4  
(Continued)

Adsorbent	Adsorbate	Adsorption capacity (mg g <sup>-1</sup> )	pH	Temp (°C)	Kinetic model	Isotherm	Reference
Cross-linked Chitosan Pine sawdust (Raw)	Indigo Carmine	–	–	25–35	–	–	[159]
	Acid Blue 256	280.3	3.5	25	Pseudo-second order, Elovich equation	Langmuir	[160]
	Acid Yellow 132	398.8	3.5	25	Pseudo-second order, Elovich equation	Langmuir	
Bentonite Untreated Alunite	Basic Blue 9 (MB)	1,667	7.9	25 ± 2	Pseudo-second order	Langmuir	[161]
	Reactive Blue 114 RR 124	2.92	2	–	–	Langmuir	[162]
	Reactive Yellow 64	2.84	10	–	–	Langmuir	
Calcined Alunite	Reactive Blue 114 RR 124	5	10	–	–	Langmuir	
	Reactive Blue 114 RR 124	170.7	2	–	Pseudo-second order	Langmuir	[162]
	Reactive Yellow 64	153	10	–	Pseudo-second order	Langmuir	
	Reactive Yellow 64	236	10	–	Pseudo-second order	Langmuir	

## 5. Discussion and conclusion

It can be observed that the society has become more and more sensitive toward the protection of the environment in last 2–3 decades. Hence, it concerns about the potential adverse effects of the chemical industry on the environment. The wastewater containing any toxic compounds is harmful to environment as well as human being. Dyes are highly visible material and even minor release into the environment may cause the appearance of color. In the case of dyes, even below 1 ppm has a potential toxicological threat. There is quick requirement to minimize environmental release of color especially in textile industries as they are main user of dyes. An alternative approach is effluent treatment methods to remove color. These methods inevitably add to the overall process cost. More than 100,000 commercially available dyes are existed and more than  $10 \times 10^5$  tonnes per year are produced annually in textile and allied industries. Wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light. A synthetic dye in wastewater cannot be efficiently decolorized by traditional methods. This is because of the high cost and disposal problems for treating dye wastewater at large scale. At even low levels of dye concentration, it adversely affects aquatic and human life. They have different chemical structures which makes them difficult to separate from the wastewater or effluent.

Many methods in the category of physical, chemical, and biological are available for the removal of dyes from the textile industry effluent. These methods are as follows: adsorption, membrane filtration, ion exchange, electro kinetic coagulation, coagulation–flocculation, adsorption on active carbon powder coupled with coagulation process, RO, nanofiltration, ultrafiltration/ microfiltration, fenton's reagent, ozonation, photochemical NaOCl, electrochemical destruction, standard biological degradation, etc. The removal of dyes can be quantified in terms of COD reduction and color removal.

All of these techniques have their own advantages and disadvantages. Biological treatment is often the most economical alternatives 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 for the treatment of industrial effluents because many micro-organisms such as bacteria, yeasts, algae, and fungi are able to accumulate and degrade different pollutants. However, their application is often restricted because of technical constraint. As 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. Further, biological treatment is incapable of obtaining satisfactory color elimination with current conventional biodegradation processes.

Chemical methods include coagulation or flocculation combined with flotation and filtration, precipitation–flocculation, electroflotation, electrokinetic coagulation and conventional oxidation methods include 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.

Physical methods are also widely used, such as membrane–filtration processes (nanofiltration, RO, and electro dialysis) and adsorption techniques. The major disadvantages of the membrane processes is that they have 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 sorbent is inexpensive and does not require an additional pretreatment step before its application. Adsorption is a well-known equilibrium separation process and an effective method for wastewater treatment applications. Adsorption has been found to be superior due to other techniques in terms of initial cost, flexibility and simplicity of design, ease of operation, insensitivity to toxic pollutants, etc. The extensive research has been available on this field which has brought a wide range of adsorbents in reach of industries.

Among various available processes, adsorption is the most promising and convincing due to its simplicity, efficiency, and cost-effectiveness. A lot of work has been done for the removal of various dyes using different types of adsorbents. Activated carbon is the most conventional adsorbent which is used. Few studies on the removal of dyes using various CAC and synthesized activated carbon are summarized in Table 3. Apart from activated carbon, low-cost adsorbents are also tried by various researchers for removal of dye. In this category, most of the adsorbents are synthesized using agriculture waste. Few studies on the removal of dyes using various low-cost adsorbents

are summarized in Table 4. The effectiveness of various adsorbents is discussed based on the current applications and is compared. If carefully selected the natural or waste material can also serve as an excellent adsorbent, whereas, its processing charge is minuscule with respect to any commercial or derived adsorbent. The industries with wastewater treatment plants are getting ready for an age of natural and waste converted adsorbents to take over the market.

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