Review on Dye Removal from Its Aqueous Solution into Alternative Cost Effective and Non-Conventional Adsorbents

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Abstract

Dyes are complex organic compounds which are used by various industries to colour their products. These dyes are purged from various industrial sources such as textile, cosmetic, paper, leather, rubber and printing industries. Wastewater effluents contain dyes which may cause potential hazards to the environment. Some of these dyes are toxic, carcinogenic and can cause skin and eye irritation. Therefore, many researchers have been studying the effectiveness of dyes removal from aqueous solution by different separation methods. Different separation techniques have been used for the treatment of dye-bearing wastewater such as adsorption, coagulation/flocculation, advanced oxidation technologies, ozonation, and membrane-filtration, aerobic and anaerobic degradation. All dye separation techniques have their own limitation in terms of design, operation efficiency and total cost. This review paper provides extensive literature information about dyes, its classification and toxicity together with various treatment methods into dye adsorption characteristics of several non-conventional cost effective sustainable adsorbents. The mechanism and the effects of various physio-chemical process parameters on dye adsorption are presented here.

Keywords: Dye adsorption; Kinetic study; Adsorbents; Activated carbon; Agricultural by-products

Introduction

Dye bearing effluent is a significant source of water pollution. Dyes are used in textile, paper, printing, carpet, plastic, food and cosmetic industries. Dyes are mainly classified into cationic, anionic and non-ionic dyes. The removal of anionic dyes is to be considered as the most challenging task as they are water soluble and produce very bright colours in water with acidic properties. It has been estimated that the total dye consumption in textile industry worldwide is more than 10,000 tonnes per year and about 10–15% of these dyes are released as effluents during the dyeing processes [1, 2]. These effluents can cause potential pollutants to human beings and to aquatic life. Various Physical, Chemical and Biological separation technologies are used in the removal of these effluent[3]. All of these methods have their own advantages and disadvantages. However, adsorption process is considered to be a very effective physical separation technique in wastewater treatment in terms of simplicity of design, ease of operation and insensitivity to toxic substances provided adsorbents are locally available with little or no value[4-7]. The current research seeks various cost effective sustainable alternative to commercial activated carbon adsorbents therefore, research has been grown into this direction since last decades. Various review articles in the removal of different dyes are available such as article by Salleh et al., (2011), Yagub et al., (2014) and Srinivasan and Viraraghavan., (2010) [8-10] but sometime these review article is very much specific in specific dye removal research. However these articles are very much helpful to develop our current review article which is more general and up-to-date dye adsorption information by various adsorbent has been compiled here. Another new aspect of this review article is to compile the scattered available literatures in dye removal by various physiochemical, chemical and biological separation techniques. Also, this review article focuses on dye adsorptive mechanism under various physicochemical process parameters.

Dyes sources and their classifications

Dye's molecules are consisted of chromophores and auxochromes components where chromophores (OH, NH2, NHR, NR2, Cl and COOH) are responsible for the production of colours and auxochromes (NO2, NO, N=N) enhance the
affinity of the dye toward the fibres[9]. Dye bearing effluents from these industries are characterized by its high colour, organic content and hazardous as well. Dyes can be produced from natural or synthetic sources as shown below.

### Natural dyes

Natural dyes are organic compounds used to colour various products. In Prior to the year of 1856, natural dyes are extracted from plants, animals, insects and minerals sources. Natural dyes are such as Turmeric, Weld, Onion, Jackfruit, henna, eucalyptus are used in the early textile industry. Due to the increase in population and industrial activities, natural dyes do not meet the industrial demand and their applications have been limited mainly in food industry. The most common natural dyes used in textile industry are presented in Table 1 along with their scientific names and chemical structures.

### Synthetic dyes

The first synthesis dye was discovered by William Henry Perkin in 1856. Dye effluents are produced because dyes do not have a complete degree of fixation to fiber during dyeing and finishing processes[11]. Dye based effluents can cause a serious hazards to the water stream and environment due to their synthetic origin and complex molecular structures which decrease their ability to biodegrade. There are various types of dyes used in various industries such as acid dyes, reactive dyes, basic dyes, azo dyes, direct dyes, vat dyes and disperse dyes[12]. All dyes are water soluble except disperse dyes and vat dyes. All dyes contain traces of metals such as copper, zinc, lead, chromium and cobalt in their aqueous solution except vat and disperse dyes. Dye bearing effluents from these industries are characterized by its high colour, organic content and hazardous as well. It is estimated that more than 100,000 commercial dyes are known with an annual production of more than 7x10^5 tonnes per year[2]. Dyes are broadly classified into cationic, anionic and non-ionic dyes. Anionic dyes include various dyes’ groups such as acid dyes, reactive dyes, azo dyes.
and direct dyes while cationic dyes are the basic dyes. Dye's classifications and their applications are presented in Table.2.

Dyes and their toxicity effects

Cationic dyes are also called basic dyes due to the presence of positive ions in the molecule's structure. Basic dyes are water soluble and they are highly visible in water even at very low concentration. Basic dyes consist of monoazoic, diazoic and azine compounds [13]. Cationic dyes are used to colour wool, silk, nylon, mod-acrylic and polyester materials. Cationic functionality is found in various types of dyes such as cationic azo dyes, methylene dyes, anthraquinone, di- and tri-arylcarbeneum, phthalocyanine dyes, polycarbocyclic and solvent dyes [9]. Basic dyes are toxic and can cause allergic dermatitis, skin irritation, mutations and even cancer [14]. Also, cationic dyes can cause increased in heart rate, shock, vomiting, cyanosis, jaundice, quadriplegia, heinz body formation and tissue necrosis in humans [15]. Anionic dyes have negative ions due to the excess presence of the OF- ions in aqueous solution. Anionic dyes are water soluble and they include acid dyes, azo dyes, direct dyes and reactive dyes. Reactive dyes attach to their substrates by a chemical reaction (hydrolysis of the reactive groups in the water) that forms a covalent bond between the molecule of dye and that of the fibre[12]. Anionic dyes removal is the most challenging task as they produced very bright colours in water and show acidic properties. Reactive dyes contain reactive groups such as vinyl sulphone, chlorotriazine, trichloropyrimidine, and difluorochloropyrimidine that covalently bonded with the fiber during the dyeing process [16]. Moreover, azo dyes represent the largest class of reactive dyes used in the textile industry followed by anthraquinone and phthalocyanine classes [17]. Azo dyes have the largest variety of dyes and under anaerobic conditions, the dye's linkage can be reduced to form aromatic amines which are colourless but can be toxic and carcinogenic [18]. It was estimated that 130 of 3,200 azo dyes in use can form carcinogenic aromatic amines during degradation process [18].

Dye separation techniques

Wastewater effluents contain synthetic dyes which may cause a potential hazard to the environment. Due to the environmental and health concerns associated with the wastewater effluents, different separation techniques have been used in the removal of dyes from aqueous solutions. The separation methods can be divided into physiochemical, chemical and biological methods. Each separation technique has its own limitation in terms of design, dye separation efficiency and total cost. A summary of dye removal separation techniques is presented with their advantages and disadvantages in Table.3.

Physiochemical separation technique

There are various types of physiochemical methods used in the removal of dyes as part of water and waste water treatments.

Adsorption

The process of adsorption involves the ions, atoms or molecules of the adsorbate to transfer and adhere to the surface of the adsorbent creating a thin film. The adsorbate can be in gas, liquid or dissolved solute phases. Adsorption technique can be divided into physical and chemical adsorption. Physisorption is another term of physical adsorption process and it is controlled by physical forces such as Van der Waals forces, hydrophobicity, hydrogen bond, polarity, static interaction, dipole –dipole interaction, H- I interaction etc. In the physical adsorption, pollutants get accumulated on adsorbent surface by the above mentioned interactions while chemical adsorption (Chemisorption or Langmuir adsorption) is defined when the adsorbate is chemically bound to the adsorbent's surface due to the exchange of electrons[19]. The extent of adsorption depends on the nature of adsorbate such as molecular weight, molecular structure, molecular size, polarity and solution concentration. It is also depends on the surface properties of adsorbent such as particle size, surface area, surface charge etc. [20], charge etc. [20]. Adsorption process is a very effective separation technique and it is considered to be superior compared to other available techniques for wastewater treatment in terms of initial cost, simplicity of design, ease of operation and insensitive to toxic substances [4, 21]. The efficiency of adsorption process depends on the physical and chemical properties of the adsorbents and adsorbate. Adsorbent's selectivity is based on the adsorption capacity, surface area, availability and total cost. Commercial activated carbon is used as an adsorbent in the removal of dyes. However due to the high cost associated with its production and regenerat-

| Separation Technique | Advantages | Disadvantages |
|----------------------|------------|---------------|
| **Physiochemical**   |            |               |
| Adsorption           | High adsorption capacity for all dyes. | High cost of adsorbents. Need to dispose of adsorbents. |
| Ion exchange         | No loss of sorbents. | Not effective for disperse dyes. |
| Membrane filtration  | Effective for all dyes with high quality effluent. | Suitable for treating low volume and production of sludge. |
| Electrokinitic coagulation | Economically feasible. | Need further treatments by flocculation and filtration and production of sludge. |
| **Chemical**         |            |               |
| Fenton reagent       | Effective process and cheap reagent. | Sludge production and disposal problems. |
| Oxonation            | No production of sludge. | Half-life is very short (20 min) and high operational cost. |
| Photocatalyst        | Economically feasible and low operational cost. | Degrade of some photocatalyst into toxic by-products. |
| **Biological**       |            |               |
| Aerobic degradation  | Efficient in the removal of azo dyes and low operational cost. | Very slow process and provide suitable environment for growth of microorganisms. |
| Anaerobic degradation| By-products can be used as energy sources | Need further treatment under aerobic conditions and yield of methane and hydrogen sulfide. |

Table 3: The advantages and disadvantages of various dye removal techniques [10, 11]
Raw and treated agricultural solid wastes in dye removal: The cost high associated with use and regenerate of commercial activated carbon (CAC) in adsorption leads the researchers to investigate and develop cost effective sustainable agricultural waste adsorbents. Agricultural wastes usually have high molecular weight due to the presence of lignin, cellulose and hemicelluloses components [9]. These solid wastes are renewable sources and are available in large quantities with little or no value and often cause a disposal problem. The use of agricultural waste helps to reduce the waste and produce a better waste minimization plan. Various cost effective adsorbents have been successfully used in the removal of textile dyes from wastewater such as coffee waste, eucalyptus wood, Organo-attapulgite, pellets of trametes versicolour, pine cone, palm shell etc. [31-33]. Table 4 presents the compilation results on various agricultural by-product adsorbent in the removal of dyes from aqueous solution. Readers are encouraged to go through review articles on the removal of dyes by agricultural wastes adsorbents by Salleh et al., (2011) and Yagub et al., (2014), [8, 9].

Biomass based activated carbon in dye removal: Activated carbon (AC) is produced from a non-renewable source such as coal and it is used as an adsorbent in the removal of toxic dyes by adsorption. The effectiveness of this versatile adsorbent is due to its high external surface area, pores structure, high adsorption capacity and high degree of surface reactivity. Micropores AC are responsible for the active sites for dyes or ions adsorption while mesopores AC act as transportation routes [34]. Activated carbon is produced in granular and powder forms. Activated carbon has various effluent treatment applications in oil and gas, food, chemical industries, solvent recovery, air pollution control and in hydrometallurgy industry for the recovery of gold and silver [35]. In the recent years, growing research interests are focusing on the agricultural solid residual biomass based AC. Biomass waste offers cost effective and renewable source for the production of AC. These waste materials have little or no economic value and often present a disposal problem [21]. Therefore, there is a need to valorise these low cost by-products. This conversion into AC will add economic value, help to reduce the cost of waste disposal and provide a potentially inexpensive alternative adsorbent to commercial activated carbons. Ribas et al., (2014) compared the effectiveness of reactive violet dye removal using a cocoa based activated carbon and commercial activated carbon [36]. Biomass based activated carbon is synthesized by either a physical or a chemical activation method. Previous studies on the use of commercial activated carbon (CAC) and biomass based AC in the removal of different dyes is presented in Table 5.

Chemical activation of adsorbents: Reagents such as phos- phoric acid, zinc chloride, potassium hydroxide, potassium carbonate and sodium hydroxide are used in the chemical activation of carbon under different conditions [37, 38]. Alkali hydroxides and zinc chloride are not preferred due to their corrosive natures and the harmful effects associated with the disposal [39]. Potassium carbonate is used as a food addictive thus it is safe to use it as an activating agent in the production of activated carbon. AC production depends on the precursor properties, reagent used, impregnation ratio, activation time and temperature. Chemical activation has more advantages than physical activation because it is carried out in single step i.e. carbonization and activation are united at relatively lower temperature operation and higher yield [37, 38]. Various researchers [28, 30, 38-40] have successfully reported the production of chemically activated biomass based AC in the dye removal.

Physical activation of adsorbents: Physical activation method is used to improve the porosity of AC by exposing carbonaceous material to carbon dioxide gas, air mixture or steam under high temperature profile. An abundance of pores, particularly micropores, were generated after activation due to the

| Adsorbents                  | Dyes                  | Adsorption capacity qmax (mg/g) | Reference |
|-----------------------------|-----------------------|---------------------------------|-----------|
| Peroxide treated rice husk  | Malachite Green       | 26                              | [106]     |
| Raw coffee residue          | Basic blue 3G         | 251                             | [32]      |
| Coffee waste                | Tohuidine Blue        | 142.5                           | [33]      |
| Raw coffee residue          | Remazol Blue          | 232                             | [32]      |
| Pine cone                   | Congo red             | 19.18                           | [27]      |
| Acid treated pine cone      | Congo red             | 40.19                           | [27]      |
| Eucalyptus wood             | Congo red             | 66.7                            | [107]     |
| Date Stones                 | Methylene blue        | 43.5                            | [108]     |
| Palm-Trees                  | Methylene blue        | 39.5                            | [108]     |
| Palm shell                  | Reactive red 141      | 14                              | [61]      |
| Palm shell                  | Reactive blue 21      | 24.7                            | [61]      |
| Acid treated papaya seed    | Methylene blue        | 250                             | [109]     |
| Papaya seed                 | Methylene blue        | 200                             | [109]     |
| Papaya seed                 | Congo red             | 71                              | [109]     |
| Acid treated papaya seed    | Congo red             | 59                              | [109]     |
| Peanut hull                 | Reactive black 5      | 55.6                            | [110]     |
| Pine cone                   | Methylene blue        | 109.9                           | [4]       |
| Pine tree leave             | Methylene Blue        | 126.6                           | [3]       |
| Neem bark                   | Malachite green       | 0.36                            | [111]     |
| Mango bark                  | Malachite green       | 0.5                             | [111]     |
| Pine cone                   | Acid Black 26         | 62.9                            | [31]      |
| Pine cone                   | Acid Green 25         | 43.3                            | [31]      |
| Pine cone                   | Acid Blue 7           | 37.4                            | [31]      |
| Pine tree leaves            | Basic red 46          | 71.9                            | [26]      |
| palm kernel fiber           | Crystal violet        | 78.9                            | [112]     |
| palm kernel fibre           | Methylene blue        | 95.4                            | [112]     |
| Organo-attapulgite          | Congo red             | 189.4                           | [65]      |
| Garlic peel                 | Methylene blue        | 142.9                           | [113]     |
| Rice husk                   | Indigo Carmine        | 65.9                            | [62]      |
| Yellow Passion fruit        | Methylene blue        | 44.7                            | [114]     |
| Soy meal hull               | Direct red 81         | 120.5                           | [115]     |
| Soy meal hull               | Acid blue 92          | 114.9                           | [115]     |
| Soy meal hull               | Acid red 14           | 109.9                           | [115]     |
| Rice husk                   | Methylene blue        | 40.6                            | [15]      |
| Sugar cane bagasse          | Congo red             | 38                              | [116]     |

Table 4: Compilation results on the removal of various dyes by various raw and treated agricultural by-product waste adsorbent
totally soluble solution. Water droplets are slowly dispersed thermodynamically stabilise the mixture and form a clear and ter and oil phases. Surfactant and co-surfactant are used to emulsion water in oil method is a mixture of immiscible wa-
dye removal due to their super-magnetic properties. Micro-
ides nanoparticles[44-47]. Magnetite (Fe3O4) and Maghemite method has been used widely in the preparation of metal ox-
state of aggregation and preparation methods. Co-precipita-
nanoparticles strongly depends on size, surface chemistry,
20-100 nm have attracted the researcher’s attention due to their excellent magnetic properties, high surface area, high adsorption capacity, nanoparticle size and easy magnetic separa-
tion of solids after adsorption[43]. The behaviour of magnetic nanoparticles strongly depends on size, surface chemistry, state of aggregation and preparation methods. Co-precipita-
tion, mechanical attrition and hydrothermal methods are used in the preparation metal oxides. Microemulsion water in oil method has been used widely in the preparation of metal ox-
ides nanoparticles[44-47]. Magnetite (Fe3O4) and Maghemite (y-Fe2O3) are the common types of iron oxides used in the dye removal due to their super-magnetic properties. Micro-
emulsion water in oil method is a mixture of immiscible wa-
ter and oil phases. Surfactant and co-surfactant are used to thermodynamically stabilise the mixture and form a clear and totally soluble solution. Water droplets are slowly dispersed and collided in the oil and surfactant solution forming a nano reactor which is driven by the Brownian motion[48, 49]. Saha et al.,(2011) have reported the removal of different dyes such as erichrome black-T, bromophenol blue and bromocresol green using iron oxide nanoparticles which are ferromagnetic in nature at both room and low temperature[50]. Also, Zn-
Fe2O4 spinel ferrite nanoparticles has been successfully used in the removal of Acid Red 88 dye from aqueous solution by adsorption[51]. Weng et al., reported the removal of an acid dye (new coccine) from aqueous solutions using magnetic Fe3O4 nanoparticles [52]. Furthermore, porous Ni0.6Fe2.4O4 nanoparticles has been successfully synthesized and used as an adsorbent in the separation of Congo red dye [53]. These nanoparticles present high adsorption rate compared to other known adsorbents. Modified magnetic nanoparticles with aminoguanidine were successfully synthesized in the removal of Acid Green, Acid Violet, Acid Orange ,Acid Red and Methyl blue dyes [54] by adsorption.

Clay Minerals: Clays are natural aluminosilicate with the presence of small amount of metal ions and organic compounds. Clays are available as the colloidal fraction in soils, sediments, rocks and water. The use of clays is considered to be a good adsorbtion because of its large surface area, high cations exchange capacity, chemical and mechanical stability and layered structure [55]. Also, they are abundantly available at lower cost in compare to other high cost adsorbents such as commercial ac-
tivated carbon. Natural clays are usually used for the removal of cationic dyes such as methylene blue due to their natural negative charged; however modifications to the surface of clay using surfactants can change the surface charge of clay from negative to positive [24]. These modifications enhance the ad-
orption of anionic dyes. Researchers studied various type of clays in the removal of textile dyes and metal ions such as Re-
active red 120 by raw clay [24], Brilliant green dye by red clay [56], Congo red by sodium bentonite, kaolin and zeolite [57], zinc ions by kaolin [55] and Methylene blue by montmoril-
lonite clay [58]. Readers are encourage to go through a review report by Yagub et al., (2014) [8].

Inorganic materials in dye removal: Metal oxides nanoparticles, clays and minerals are also used as adsorbents in the removal of dyes from its aqueous solution.

Metal oxides nanoparticles: Metal oxides and core/shell compo-
site nanoparticles are used in wastewater treatment industry. Iron oxides nanoparticles with a particle average size of 20-100 nm have attracted the researcher’s attention due to their pH of a solution is a measure of molar concentration of hydrogen ions. Acidic solution occurs when the solution pH < 7 where a solution pH > 7 indicates a basic solution. The change in solution pH is an important parameter for solute adsorption because of change in surface characteristics of adsorbent and change in chemistry of dye. Thus, the adsorption capacity of dye depends on the pH of the solution. Generally, low pH solution results in an increase in the percentage of anionic dye removal because of the electro-
static attraction between anionic dye and the positive surface charge of the adsorbent [9]. At higher solution pH, electrostatic repulsion is found between the negatively charged surface and dye molecules, thus decreasing the adsorption capacity and percentage removal of anionic dyes [59]. From previous studies, the optimum solution pH on the removal of anionic dyes such as Congo red by nut shells charcoal [60], Acid blue 15 by Pomelo skin [59], Congo red by raw and acid modified

| Material                      | Dye                       | Adsorption capacity qmax (mg/g) | Reference |
|-------------------------------|---------------------------|--------------------------------|-----------|
| Commercial activated carbon   | Reactive Violet 5          | 517.1                          | [35]      |
| Commercial activated carbon   | Acid Red 97               | 52                             | [3]       |
| Commercial activated carbon   | Acid Orange 61            | 169                            | [3]       |
| Commercial activated carbon   | Acid Brown 425            | 222                            | [3]       |
| Commercial activated carbon   | Congo red                 | 300                            | [22]      |
| Commercial activated carbon   | Remazol red B             | 145                            | [115]     |
| Pine cone based AC            | Congo red                 | 500                            | [30]      |
| Cocoa shell AC                | Reactive Violet 5         | 603.3                          | [35]      |
| Bacl shell based AC           | Congo red                 | 98                             | [41]      |
| Waste tea based AC            | Acid blue 29              | 596                            | [28]      |
| Bamboo based AC               | Methylene blue            | 454                            | [116]     |
| Cattail based AC              | Neutral red               | 192                            | [117]     |
| Cattail based AC              | Malachite green           | 196                            | [117]     |
| Pomelo skin based AC          | Acid blue 15              | 444                            | [58]      |
| Pomelo skin based AC          | Methylene blue            | 501                            | [58]      |
| Date stone based AC           | Methylene blue            | 316                            | [59]      |
| Olive stone based AC          | Remazol red B             | 9                              | [115]     |
| Rice husk based AC            | Methylene blue            | 442                            | [118]     |
| Rambutan peel based AC        | Malachite green           | 329                            | [119]     |
| Rubber seed coat based AC     | Malachite green           | 227                            | [120]     |
| Myrtus communisbased AC       | Congo red                 | 19                             | [121]     |
| Pomegranate based AC          | Congo red                 | 10                             | [121]     |

Table 5: Removal of dyes by Commercial activated carbon (CAC) and bio-

mass based activated carbon (AC)
Effect of adsorbent dose: The effectiveness of various adsorbent doses on both anionic and cationic dyes removal is reported by many researchers to determine the most economical minimum dosage. In general, the dye removal percentage is increasing with the increase of the adsorbent dosage [9]. It was reported that the amount of Methylene blue dye removal by pinecone was increased from 62.9% to 97.2% with the increase of adsorbent mass from 0.01 to 0.05 g [4]. Also, that the amount of Indigo carmine dye removal by rice husk was increased from 36% to 96% with the increase of adsorbent dose from 2-20 g/L [62]. According to [63], the amount of Congo red dye removal increased from 56.3% to 99.3% for an increase in adsorbent dose from 5 to 30 g/L.

Effect of temperature: The temperature of the solution plays an important role on the adsorption capacity. If the adsorption capacity increases with increasing temperature then the adsorption is an endothermic process. The dye removal percentage of various dyes such as Congo red by modified hectorite [64], Congo red by organo-attapulgite [65] Congo red by raw pinecone and biomass based activated carbon respectively [27, 30] were increased with the increase of solution temperature. However, the dye removal of Methylene blue by pine cone [4] and Methylene blue by montmorillonite clay [58] was reported to decreases with the increase of solution temperature therefore the adsorption process is an exothermic process.

Effect of initial dye concentration and contact time: The effect of the initial dye concentration plays a significant role in the amount of dye adsorbed qt (mg/g) and percentage of dye removal. Generally, increasing the initial dye concentration leads to decrease the percentage of dye removal which may be due to the saturation of adsorption sites on the adsorbent surface [9, 30]. The amount of dye adsorption qt (mg/g) increases with increasing contact time at all initial dye concentrations as reported by various researchers [4, 22, 59]. This is so because the initial dye concentration provides the driving force to overcome the resistance to the mass transfer of dye between the aqueous and the solid phase.

Ion Exchange method

Ion exchangers are solid materials or liquid solutions which are able to absorb positively or negatively charged ions from aqueous electrolyte solutions and at the same time release other ions of equivalent amount into the aqueous solution [66]. Most synthesis resins are polymeric structures. The synthetic ion exchange materials can be classified into four main groups of solid membranes, solid sheets, organic solvent solution of liquid ion exchangers and solid particle [66]. Commercial anion exchange resins have the potential to possess excellent adsorption capacity and show high regeneration property for the removal and recovery of reactive dyes [17]. The applications of the ion exchange in the field of wastewater treatment, sugar and alcohol processing, pharmaceutical applications such as biological recovery and purification and hydrometallurgy industry [67] has been reported. Also, ion exchange is used to remove toxic dyes from wastewater such as removal of anionic dye Orange-G [16] and cationic dye Methyl violet 2B [17]. Ion exchange is a good method to separate toxic and soluble dyes from water effluents although the high capital cost associated with this process limited its use.

Membrane Filtration technique

Filtration is used to separate ion independent particles from solution. Some undesirable particles may pass into the filtrate solution depend on the pore size and thickness of the filter membrane. Filtration is used to remove dyes in the wastewater treatment. Microfiltration, ultrafiltration and nanofiltration are considered to be one of the economical and critical technologies in chemical and biochemical processing due to their availability with higher flux and lower process cost [68]. Nanofiltration membrane is a combination of reverse osmosis and ultrafiltration processes and it is used in the removal of textile dyes such as Methylene blue [69] and cotton dye effluent [70]. Nanoporous membranes with cellulose nanocrystals is also used in the removal of various dyes such as Victoria Blue, Methyl Violet and Rhodamine dyes [71]. The disadvantages of this process such as the high pressure needed, clogging of the membrane's pores and incapability to treat large volume of effluents limit its uses [72]. Also during the operation, various suspended particles such as dyes and organic matter tend to accumulate within a thin boundary layer adjacent to the membrane surface and result in membrane fouling[73]

Electrokinetic Coagulation

Electrokinetic coagulation (EC) is a physio-chemical process used in the wastewater treatment. EC technique uses a direct current source between metal electrodes such as aluminium and iron immersed in water effluent to cause the dissolution of metal plates into wastewater[74]. The metal ions form coagulated for particulates flocculating which cause metal hydroxides to precipitate and chemically adsorb dissolved contaminants[75]. EC process provides a simple, reliable and low cost method for the removal of dyes such as direct red(81) from wastewater[74], reactive blue 140 [76] and disperse red[77]. The main advantages of electro coagulation in compare to other conventional technique such as chemical coagulation are the compact of equipment used and no generation of secondary pollution [76]. The disadvantages associated with this process are the need for further treatment by flocculation and filtration and high amount of sludge produced.

Chemical Methods

Advanced Oxidation Technologies (AOTs)

Oxidation process is one of the traditional methods used for the removal of inorganics/organics from wastewater. The effectiveness of advanced oxidation technologies (AOTs) are
based on the generation of oxidizing reagent(•OH) radicals as they attack the Chromophores leading to the production of organic peroxide radicals and finally convert to CO2, H2O and inorganic salts [78]. Chemical oxidation is very effective but the efficiency strongly influenced by the type of oxidant[79]. ATOs include the use of oxidants such as chloride, ozone, Fenton and Fenton-like reagents and chlorine dioxide. Fenton’s reagent is also known as hydrogen peroxide and it is more effective if applied at acidic solution. Iron ions such as Fe+2 and Fe+3 are the most common reagents used in Fenton activation. Fenton’s reagent is cheap and easy to handle compared to other reagents. The decomposition of Fenton-like reagent is presented in the following equations [80]

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{H}^+ + \text{OH}^- \]  
\[ \text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+ + \text{OH}^- \]  
\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{H}^+ + \text{OH}^- \]

The iron(III) reacts with hydrogen peroxide to form iron (III) peroxo complex. The complex is decomposed to produce iron (II) then it reacts with hydrogen peroxide to yield the oxidant, hydroxyl radicals. The removal efficiency of this process depends on the production of the oxidant, hydroxyl radicals which exhibit higher removal percentage at higher dyes concentration. This process has its own limitations as these reagents are toxic and may cause more harm to the biological treatment system used for the post treatment than the original textile dyes [81]. Also, the large volume of sludge formation and the hazards associated with its disposal limits the use of this process in industrial scale. Previous studies of Fenton and Fenton-like reagents are used to remove textile dyes such as reactive red, acid blue and direct blue [79], acid orange and reactive blue [81] and Reactive Black 5 , Reactive Orange 16 and Reactive Blue 2 [82]. Ozonation is another type of AOT’s oxidation used in the removal of synthesis dyes from wastewater effluents. It is a very effective technology in treating wastewater and is considered to be a good method in the decolorization of textile effluents as ozone (O3) attacks the nitrogen conjugated double bonds which are often associated with colours [83, 84]. Ozonation reactions can be classified into direct reaction and indirect reaction based on the pH of the solution. The decomposition rate of ozone is affected by solution pH and initial dye concentration. At basic medium, ozone rapidly decomposes to yield the hydroxyl radical but in acidic conditions, ozone can directly react with organic substrates as an electrophile[84]. Ozonation process does not form a sludge because of complete decomposition of dyes thus reduce the toxicity of by-products [85]. However, the half-life of ozone is very short and it requires a high voltage to run a continuous ozonation process thus increases the capital cost and limits its uses in the industrial scale [86].

Photocatalyst

Photocatalyst is a process used in the removal of organics contaminations such as dyes from wastewater. It is also used in the production of hydrogen by water spilling method. Band gap can be described as a region between the valence band and the conduction band of the semiconductor. Photon energy equal or higher than the band gap energy is required to excite the electrons from the valence band to the conduction band and the movement of the electrons leave holes with positively charged ions (H+) in the valence band[87]. The positively charged holes are powerful oxidants and can destroy adsorbed organic pollutants where the electrons at the conduction band react with the oxygen molecules to form strong oxidative radicals that also cause the decomposition of organic and inorganic contaminations in wastewater [88]. Current studies are focused on the production of various photocatalyst such as cucurbit[6] ureil- polyoxometallates(CB[6]–POMs) composite, α-Keggin type polysilicon tungstate anions KH[SiW12O40] 2H2O [88], Bi-based oxyhalide Bi4TaO8I [89], Ternary nanocomposite of grapheme TiO2–Fe3O4(GTF) [90], α-bismuth molybdate α-Bi2MoO3(2) [91] and Bismuth phosphate BiPO4 [92]. Also, photocatalyst is used in the removal of dyes from wastewater such as Methyl Orange [88, 89], Reactive red and direct green [93]. Photocatalyst selection depends on dye’s chemical properties as some dyes are resistant to photo-degradation process [94]. Photocatalyst has feasible applications in wastewater treatment as it can operate at ambient temperature and pressure with complete mineralization thus reduce total operating cost [95]. On the other hand, some photocatalyst are degraded along the process and generate toxic products. Readers are encourage to go through a review article on photocatalyst water treatment technology by Chong et al., (2010)[95]

Biological Methods

Aerobic Degradation

Bacteria and fungi are the most microorganisms used in the decolourization of dyes under aerobic conditions. Bacteria are able to culture and grow more quickly than fungi as they are able to metabolize chlorinated and other organic contaminants and use them as carbon or energy source [96]. Bacteria are classified as mono-oxygenase or di-oxygenase enzymes and they are used to catalyse the incorporation of oxygen from O2 into the aromatic ring of organic compounds such as azo dyes and reactive dyes[97]. Many researchers have investigated the use of bacteria for the decolourization of dyes such as removal of Blue Beaktiv dye BB150 by lyophilised bacterial consortium[98]. The use of fungi in the removal of dyes is more effective compared to bacteria and algae. Many results have been reported such as the removal of azo dyes by Candida tropicalis [99] and acid red B by Pichia sp TCL[100]. Fungi have high capacity of biodegradation of dyes as they are able to deplete complex organic compounds by producing extracellular ligninolytic enzymes including laccase, manganese peroxidase and lignin peroxidise [99].White-rot fungi such as Dichomitus, squalens, Daedalea flavida, Irpex flavus and Polyporus sanguineus have been used widely in the decolourization and degradation of textile waste of many chromophoric groups of dyes [101]. The use of bacteria and fungi for the complete decolourization and degradation of dyes from textile effluent have the advantages of low cost process compared to other methods and the ability to complete mineralization of dyes with nontoxic by-products [102]. However, this process is not applicable for real textile wastewater treatment because it is a very slow process and provides a suitable environment for the growth of autochthonous microorganisms[72]. Sometimes the effluent temperature does not favour for microorganism enhanced dye removal. Bacteria and fungi strains commonly
used in the biodegradation of textile dyes are presented in Table 6.

| Culture                        | Dye              | Dye removal (%) | References |
|--------------------------------|------------------|-----------------|------------|
| *P. chrysosporium* fungi       | Coracryl violet  | 100             | [101]      |
| *P. chrysosporium* fungi       | Coracryl pink    | 100             | [101]      |
| *D. squaenea* fungi            | Coracryl pink    | 100             | [101]      |
| *T. versicolor* ATCC 20869      | Remozol red      | 98              | [124]      |
| *P. chrysosporium* ATCC 24725  | Remozol blue     | 95              | [124]      |
| *P. chrysosporium* ATCC 24725  | Remozol blue     | 95              | [124]      |
| *Aspergillus niger* fungi      | Direct violet    | 92              | [125]      |
| *Bacteria consortium* SKB-I    | Congo red        | 90              | [126]      |
| *C. polyzona* MUC 38433        | Acid blue 62     | 90              | [127]      |
| *Trametes species* CNPR 4783   | Remazol blue     | 89              | [124]      |
| *T. Versicolor* ATCC 20869      | Remozol red      | 85              | [124]      |
| *Bacteria consortium* SKB-I    | Blue BCC 74      | 74              | [126]      |
| *P. sanguineus* fungi          | Coracryl black   | 67              | [101]      |
| *Lyophilised bacterial consortium* | Blue Bezaktiv 150 | 62              | [98]       |
| *Trametes species* CNPR 4801   | Remazol blue     | 58              | [124]      |
| *D. flavida* fungi             | Coracryl pink    | 53              | [101]      |
| *T. versicolor* DSM 11269      | Disperse red 1   | 50              | [113]      |
| *Myrocothecium sp.* UHH 1-6-18-4 | Disperse blue 1 | 43            | [113]      |
| *S. rugosa* DSM 11372          | Reactive red 4   | 31              | [113]      |

Table 6: Bacteria and Fungi strains commonly used in dye biodegradation

Anaerobic Degradation

Anaerobic degradation process occurs in the absence of oxygen. Anaerobic digestion process is able to decompose complex organic compounds so that they can be further treated either aerobically or by other dye removal methods [96]. The biodegradation process consists of decolourization stage where the microorganism breaks the dye azo linkage of nitrogen double bond followed by second stage involves the degradation of the aromatic amines [103]. The decolourization stage occurs usually under anaerobic conditions. Researchers investigated the use of bacteria for dye reduction under anaerobic conditions such as removal of Methyl orange (MO) and Naphthol green B (NGB) by Shewanella oneidensis MR-1[104] and Reactive red by Halomonas variabilis and Halomonas glaciei [96]. The disadvantages of this process include the need for further treatment under aerobic conditions and production of toxic by-products. Thus a combination of anaerobic and aerobic process is recommended for the biodegradation of textile dye.

Conclusion and Future recommendations

An extensive literature information on various dye removal techniques have been discussed here. Further a wide range of adsorbents such as raw and treated agricultural by-products, activated carbon, biomass-based activated carbon, biosorbents, various other inorganic oxides, and clay minerals in the removal of dyes from aqueous solution has been reviewed here. The mechanism and the dye adsorption behaviour of various adsorbents under various physio-chemical process parameters have been critically analysed. This comprehensive review analysis identified few research gaps for which further studies required. Actual colour bearing effluents contains mixed dye pollutants including presence of salts. Therefore much work is necessary to predict the performance of dye adsorption from real industrial effluents under wide range of operating conditions. No literature is available to apply the well-developed surface reaction based dye adsorption model to obtain the effect of ionic strength or solution pH on adsorption.

In most of the reported studies, few attempts were made to relate the characterization results with the performance of adsorbents for the removal of dyes from aqueous solution under various physico-chemical conditions. Leaching of industrial wastes, agricultural solid wastes in water is very important in order to see the dissolution of the various substances present in the wastes. This interference will lead to erroneous results in the adsorption experiments. Therefore more research work should be performed in this direction.

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