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Review

Removal of Azo Dyes from Aqueous Effluent Using Bio-Based Activated Carbons: Toxicity Aspects and Environmental Impact

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Abstract: Rapid growth in various industrial fields has introduced a series of new environmental risks. The textile industry is one of the major industries that is influenced by rapid advancements in technological sectors. The development in textile dying technologies has presented new types of dyes that are toxic to the ecosystem. Azo dyes are the main artificial dyes used in textiles, food, and other applications. Typically, these dyes are introduced into the environment as wastewater discharged from factories. The discharged influence penetrates the ecosystem and causes deadly diseases to human and animals. Several studies present activated carbon as a proper solution to eliminating the presence of azo dyes in the environment. However, various types of azo dye have different properties and chemical structures. Thus, there is a crucial need for more studies on the application of activated carbons to eliminate the presence of azo dyes in the environment. This paper discusses the toxic effects of azo dyes on the environment and human health. Moreover, this work presents a general review of the preparation of activated carbon and the parameters that influence the adsorption performance.

Keywords: activated carbon; azo dye; toxicity; wastewater; lignocellulosic biomass

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1. Introduction

The significant development of industrial sectors has led to the formation of several new synthetic substances such as dyes and pigments. In scientific terminology, dyes are types of colorants that have high solubility in a chosen medium. In contrast, pigments are insoluble colorants [1]. Moreover, dyes are organic chemicals with a molecular structure that can reflect light within the visible spectrum. The textile and paint industries are mainly responsible for the release of dyes and pigments in the aqueous system. It is estimated that 7.5 metric tons of dyes are discharged annually into the ecosystem [2]. Increasing amounts of dye are released annually, generating textile waste. Recently, various studies have been conducted on different types of synthetic chemical substances to create dyes with high resistivity to light, humidity, sweat, oxidizing agents, and microbes [3]. As a result, the natural decomposition of textile wastes has become strenuous for the ecosystem. Textile wastes contain several environmental contaminants, such as fabrics, microplastics, surfactants, heavy metals, auxiliary compounds, toxic dyes, etc. [2,4].

The industrial applications of dyes are influenced by the chemical structure and properties of the manufactured dye. In general, the structure of dyes consists of aromatic rings connected with different types of functional groups containing π-electrons. The presence of the π-electron is associated with the absorbance of light within the spectrum of 380–700 nm (Figure 1). Chromophores and auxochrome are considered as the primary groups that influence the properties of synthetic dyes. Chromophores encapsulate the atoms that absorb the light energy, whereas auxochrome changes the color of the dye [5].

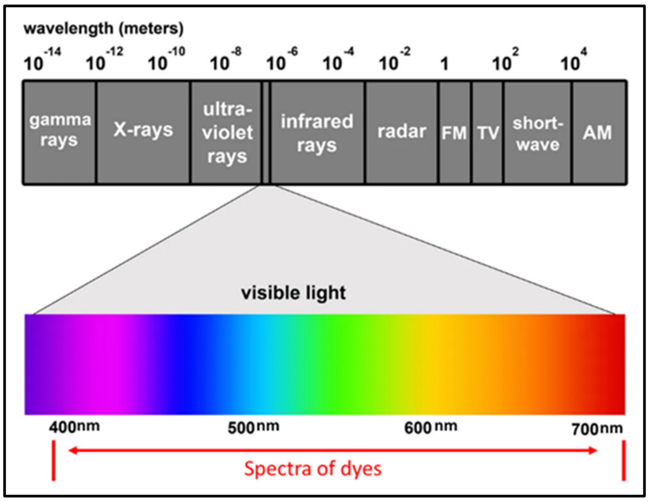

Figure 1. The visible spectrum of colored dyes.

2. Classification of Dyes

The functional groups play a pertinent role in influencing the chemical and physical properties of the dyes. The structure of the dyes is complicated due to the presence of various cationic and anionic groups attached to the aromatic rings. Nevertheless, the complex structure of the dyes is the basis of a classification used by several studies (Figure 2).

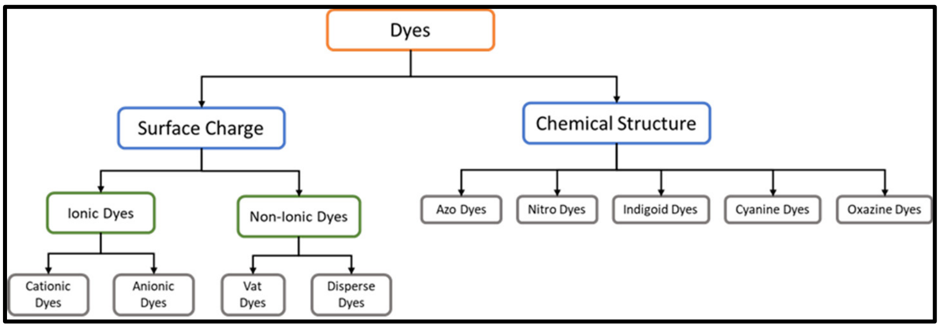

Figure 2. The general classification of dyes.

Generally, dyes can be classified according to surface charge or chemical structure. The primary classes of dyes are further divided into ionic and non-ionic dyes based on the type of ionic charge. Depending on chemical structure, the dyes can contain nitro, azo, indigoid, quinone-imine, cyanine, oxazine, diarylmethane and phthalein groups [2]. Ionic dyes, which involve cationic and anionic dyes, are the most used types of dyes. Indeed, anionic dyes are frequently adopted in the textile field due to their tendency to form covalent bonds with the surface of fabrics [2]. Conversely, cationic dyes have limited applications as they are biologically active dyes. Thus, cationic dyes are typically used for biomedical applications such as tumor detection [2]. The anionic dye family includes azo dyes, nitro, anthraquinone, nitroso, etc. However, cationic dyes contain azine, xanthene, oxazine, azo, anthraquinone, cyanine, acridine, etc. Generally, ionic dyes are carcinogenic. However, anionic dyes have higher toxicity due to their tendency to cause mutagenic diseases such as allergies and asthma [2,6].

Further classification of dyes is illustrated by Liu et al., 2020, in which dyes are categorized into two classes according to chemical structure and application [7]. The chemical structure class includes azo dyes, anthraquinone dyes, indigo dyes, phthalocyanine dyes, sulfur dyes, Jia Chuan dyes, triaryl methane dyes, and heterocyclic dyes. On the other hand, the application class involves dyes such as reactive dyes, acid dyes, direct dyes, insoluble azo dyes, insoluble vat dyes, soluble vat dyes, sulfur dyes, acid mordant dyes and acid medium dyes, oxidation dyes, polycondensation dyes, disperse dyes, basic dyes, and cationic dyes, fluorescent dyes, fluorescent brighteners [7]. Among the several types of synthetic dye, azo dyes are thecommonly used for industrial applications. The high toxicity of the azo dyes is driven by the presence of amin and benzidine compounds, which cause carcinogenic diseases [7].

2.1. Structure and Properties of Azo Dyes

Azo dyes are the most prevalent chemical dyes used intensively in the textile industry. Indeed, it is estimated that more than 50% of all dyes used in the industry are azo dyes, and this percentage is also increasing [8]. Thus, most dyestuffs used in the textile industry belong to the azo dyes family. The synthesis of azo dyes revolves around two methods, diazotization and coupling [2,3,8]. The structure of the azo dyes is composed of one or more azo bonds ($-N{=}N-$) connected to one or multiple aromatic rings [8–10]. Various modification techniques are adopted during the synthesis process to alter the coloration properties of the azo dye. Moreover, modification techniques are used to modify the particle size to enhance the dispersibility [8]. Azo dyes are used widely in paper manufacturing, textile industries, cosmetics, and printing due to their simple modification techniques.

According to Benkhaya et al., 2020, azo dyes can be classified into two classes based on the number of azo linkages and reactive functional groups [8]. Azo dyes can be prepared through different methods, such as oxidation of primary amines, reduction of nitroaromatic compounds, condensation of hydrazine and quinones, etc. [8]. Nevertheless, the primary approach to synthesizing azo dyes is via diazotization and coupling. Essentially, aromatic primary amine is diazotized and coupled with amine or phenol as electron-rich nucleophiles [2,3,8]. During azo dye synthesis, chemicals with aromatic heterocycles, benzene rings, or aliphatic groups are added to form bonds with azo groups to obtain the desired color of the dye [8]. In addition, the chemical structure of azo dyes consists of solubilizing, chromophore, and auxochrome groups, forming a covalent bond with several types of textile substrates. Their physicochemical properties and the simplicity of their synthesis are the main factors behind the intensive use of these dyes in various industries.

Anionic azo dyes have a strong tendency to form covalent bonds with synthetic fibers, cellulosic fibers, and protein fibers. The strong tendency is influenced by the presence of different functional groups that can bind with the hydroxyl groups in cellulosic fibers or amine groups in polyamide fibers [7]. Despite the behavior of azo dyes of forming bonds with several types of fabrics, the reaction between the fabrics and dyes is time consuming. Therefore, a huge percentage of used azo dyes do not stick to the surface of fabrics during the dying process. As a result, an excessive number of azo dyes are discharged into the ecosystem in the form of polluted water [9]. Typically, water contaminated with azo dyes is released into natural water resources such as rivers, coastal areas, and groundwater reservoirs [2,3,8]. As a result of easy accessibility and low cost, natural water resources are used as disposal areas. Generally, azo dyes are highly durable and do not degrade rapidly due to their robust chemical structure. As a result, the natural decomposition of azo dyes has a detrimental effect on the ecosystem.

Nonetheless, an enormous amount of discharged industrial effluents worldwide contains a high percentage of azo dyes [3,9]. In some countries, toxic dyestuff waste is discharged into coastal areas, destroying the aquatic ecosystem. Indeed, industrial effluents containing a high percentage of azo dyes are considered one of the primary xenobiotic compounds affecting the water ecosystem [2]. Discharging water contaminated with azo dyes directly into natural water resources can also affect the soil ecosystem. Hence, azo dyes can reach farming areas and leak into the food chain and the human body. The environmental concerns about the mutagenic and carcinogenic effects of azo dyes have drawn the attention of several researchers and institutes [10–12]. The environmental pollution of toxic dyes and dyestuffs is monitored by the Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD), established in 1974 [13]. The primary goal of ETAD is to protect human health and the environment from dyestuffs by minimizing the amount of discharged contaminated water in the ecosystem. The acceptable standards for the daily consumption of dyes vary according to the type of dye and its physio-chemical properties. Ionic dyes are extremely toxic to the environment, and prolonged exposure to dyes through ingestion can cause severe health effects on the human body [7].

2.2. Toxicity Aspects of Azo Dyes

Industrial applications are the primary reason behind excessive dye manufacturing. Many developing countries receive benefits directly from the development of the textile industry, which is one of the factors promoting dye production. [14]. The dyeing of textiles has been practiced in India for centuries and is believed to be the oldest art form in the world. Currently, the textile industry is dominated by countries like China, Bangladesh, and India. The global clothes and fashion market is worth around 1.7 trillion dollars [14]. Although the economic aspects of the textile industry are significant to many countries, the cost of these benefits impacts the environment and human health. In other words, the negative environmental and health impacts are the actual cost of the enormous growth of the dye industry. The global textile industry consumes a huge amount of water and discharges several types of contaminants. It is estimated that 10–25% of dyes used in the textile industry are lost during the dying process. In addition, 2–20% of the dye wastes are discharged directly into natural water resources [15,16].

2.3. The Environmental Impact of Azo Dye

Generally, azo dyes are almost non-biodegradable due to their complex chemical structure. Therefore, when azo dyes are discharged as aqueous effluents into the environment, they can cause severe damage to the ecosystem in the long and short term. The presence of azo dye in polluted water can increase the biological oxygen demand (BOD) and chemical oxygen demand (COD) [3,15–17]. Essentially, azo dyes reduce the penetration of the light into the aquatic system and therefore interrupt the photosynthesis process. Moreover, the presence of azo dyes in the aquatic environment changes the pH level and causes disintegration of organic and inorganic chemicals. Despite the prolonged existence of dyes in human history, the knowledge of the xenobiotic and recalcitrant nature of synthetic dyes such as those of the azo family is limited [17]. Despite this, the toxicity of azo dyes appears in a variety of forms, since it is not confined to a particular ecosystem. Table 1 summarizes the environmental and health impacts of azo dyes. The ecosystems are strongly interconnected, leading to the diffusion of azo dyes from one ecosystem to another. The environmental impact of toxic dyes is illustrated by Figure 3.

Table 1. Environmental and health impacts of common dyes.

Dye Classes	Environmental and Health Impact	Example	Ref.
Azo	-Cause bladder and liver cancer. -Reduced fertility of male and female mice. -Increase the chemical oxygen demand (COD).	-Tartrazine -Congo Red -Sudan Red -Sunset Yellow	[1]
Anthraquinone	-Bind to enzyme and protein fibers -Cause inhabitation of blood albumin. -Increase the chemical oxygen demand (COD).	-Alizarin Red S -Reactive Brilliant Blue R -Reactive Blue 4	[1]
Acridine	-Cause damage to DNA structure. -Have mutagenic effects. -Increase the chemical oxygen demand (COD). -Inhibit the growth of some microbes.	-Basic Yellow 9 -Acridine Orange	[2,3]
Indigoid	-Increase the chemical oxygen demand (COD). -Inhibit the growth of some bacteria. -Extremely slow degradation in the environment	-Indigo Carmine -Ciba Blue 2B	[4]
Phthalein	-Increase the chemical oxygen demand (COD).	-Thymolphthalein -Phenolphthalein -Dixylenolphthalein	[5]
Triphenylmethane	-Increase the chemical oxygen demand (COD).	-Malachite Green -Crystal Violet -Light Green SF	[6,7]
Xanthene	-Increase the chemical oxygen demand (COD). -Inhibit enzymatic activities.	-Rhodamine 6G -Rhodamine 123 -Fluorescein	[8]

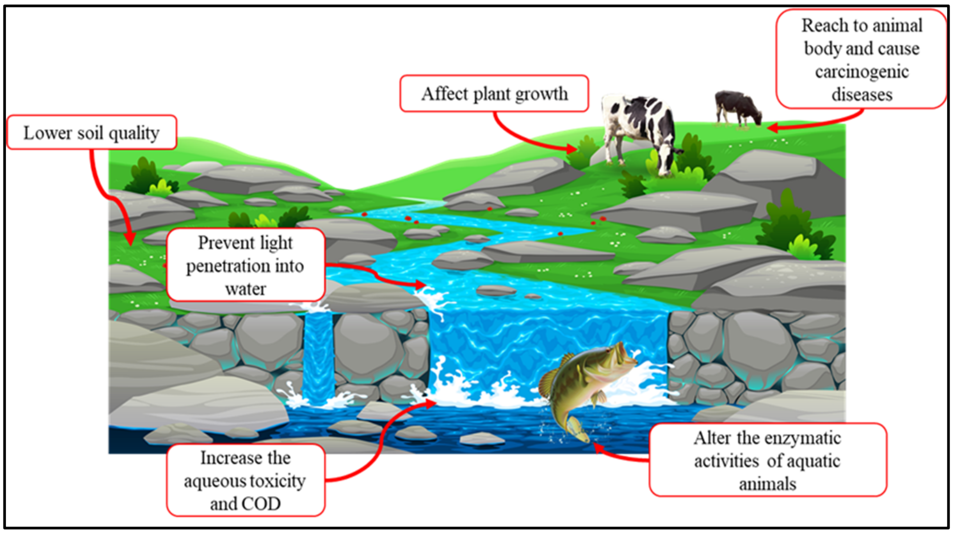

Figure 3. The environmental impacts of toxic dyes.

The interactions between dyes and several types of adsorbents and molecules in medium are mainly influenced by the dissociation constants and pKa and pKb values [10,11]. The pKa and pKb values of dyes will contribute to the reaction between the functional groups on the surface of the solid adsorbent and solutions. pKa and pKb values vary according to the type of the dye. For instance, the azo dyes typically have a pKa value between 4 and 5. Thus, azo dyes can partially disassociate in neutral solutions. Because of the impact of pKa and pKb values on the adsorption behavior, several studies have been conducted under different conditions on azo dyes. One study showed that polymeric composites can be used for the removal of methylene blue dye [10]. The study used mathematical models to demonstrate the impact of pKa values on the adsorption mechanism. According to the study, pKa value impacts the interaction of methylene blue with the functional groups where the nitrogen atoms present in the dye structure are reactive. Thus, methylene blue exhibited three chemical forms, mono-protonated (MBH), di-protonated (MBH^{2+}), and tri-protonated ($MBH_3{}^{2+}$), for $2.6 < pKa < 8.33$, and $pKa < 2.6$, respectively. Methylene blue becomes negatively charged at pKa above 8.33. As a result, the new forms of methylene blue interacted with the adsorbent through electrostatic attraction [9].

2.4. The Health Impact of Azo Dyes

The recalcitrant and xenobiotic natures of azo dyes can be shown to impact human and animal health in the form of severe pathologies. Indeed, azo dyes are considered carcinogenic and mutagenic organic chemicals [17–27]. Short-term exposure to azo dyes does not significantly impact human and animal health [18]. In contrast, long-term exposure to toxic dyes increases the bioaccumulation of these chemicals on human and animal bodies, causing several types of deadly diseases [22–27]. Typically, azo dyes reach human and animal bodies through interaction with the contaminated environment. Bioaccumulation of azo dyes occurs over time through oral exposure or inhalation in polluted ecosystems [17]. From the environmental perspective, humans are exposed to azo dyes from contaminated agricultural crops, aquatic biota, and air (Figure 4). Several toxic compounds, such as benzidine and amin, are diffused into the environment through azo dyes in contaminated water. Indeed, benzidine and amin are associated with carcinogenic diseases such as bladder cancer, intestinal cancer, and skin cancer [17].

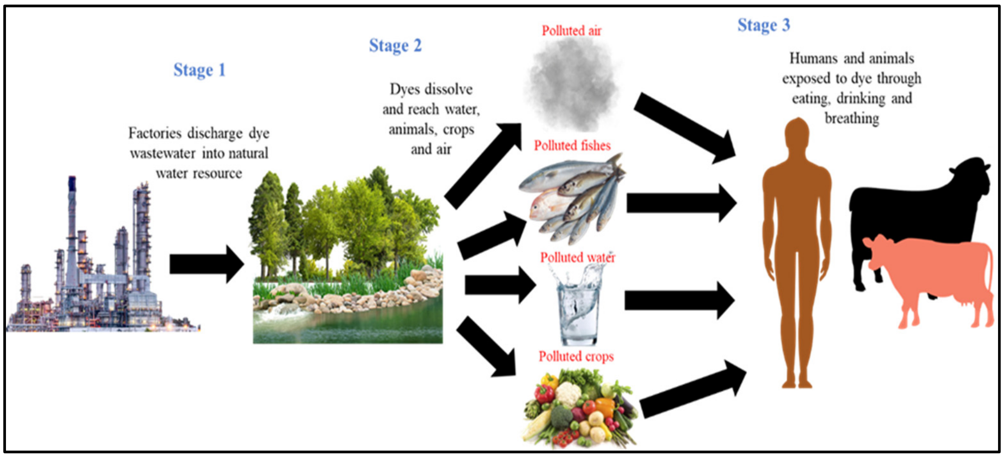

Figure 4. Sources of human exposure to Azo dyes.

Above all, exposure to azo dyes via ingestion can lead to inhibition of enzymatic activities and severe damage to the central nervous system [3,17]. Besides humans, animals are also affected directly due to the contamination of water containing azo dyes (Figure 5). For instance, one study reported the detection of bladder tumors in dogs exposed to aromatic amines discharged from azo dyes [3]. Other studies revealed that long-term exposure of rats to an azo dye known as acid yellow 36 (metanil yellow) could cause toxic hepatitis and critical damage to the brain [14,26]. A further study was conducted on goats exposed to metanil yellow through contaminated food and water. The study found that metanil yellow can alter enzymatic activities and damage the heart tissue, causing cardiotoxicity [27]. In recent decades, several studies have been conducted to illustrate the environmental and health impacts of azo dyes. These studies aim to show the critical effects of consuming azo dyes and provide a brief analysis of the techniques adopted to eliminate the presence of azo dyes in the environment.

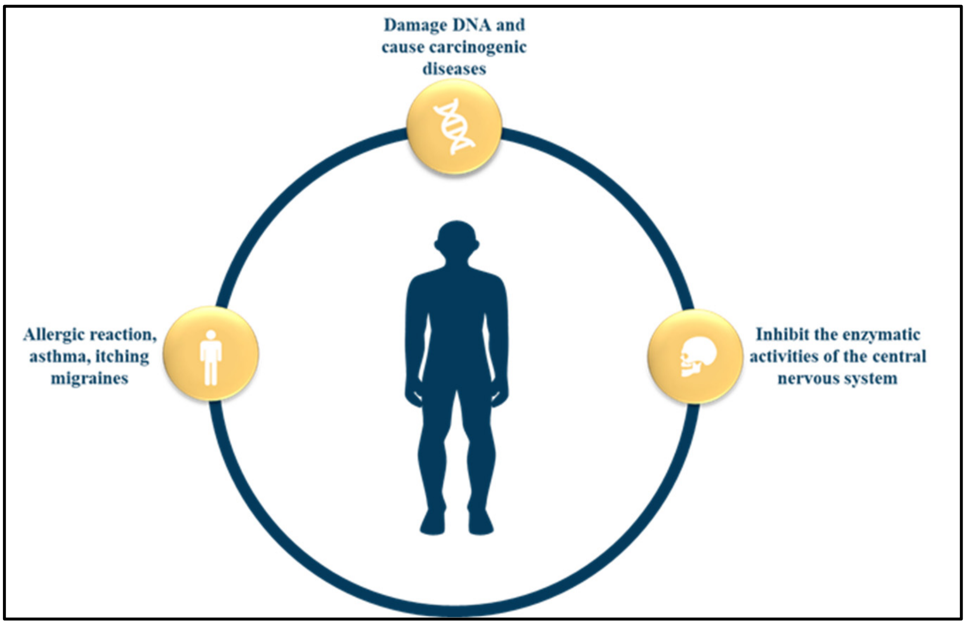

Figure 5. The health impact of azo dyes on the human body.

Researchers conducted a study on the effect of azo dyes in the Noyyal river, India [2]. The study revolved around the impact of azo dyes on microbial communities and bacterial diversity around the river and agricultural areas. The study reported a dramatic increase in the biological activities of bacteria and microorganisms in areas with a high percentage of azo dyes. Moreover, the study revealed that prolonged exposure to azo dyes had increased the abundance of *Saccharibacteria* (TM 7) and *Proteobacteria* by 36.4% and 25.4%, respectively. Although these bacteria reduce the percentage of azo dyes via consumption, they are considered extremely toxic to human health and the environment. The azo dyes increase the percentage of *Saccharibacteria* dramatically, which causes an imbalance in the ecosystem. *Saccharibacteria* is also associated with several periodontal diseases [28].

Tartrazine is a yellow anionic azo dye used in many applications (Figure 6). Certainly, tartrazine is used intensively in the textile, food, cosmetics, and pharmaceutical industries. Tartrazine dye has several commercial names, such as yellow alimentary 4, yellow acid 23, (4E)-5-oxo-1-(4-sulphonatophenyl)-4-[(4-sulphonatophenyl) hydrazono]-3-pyrazole carboxylate, or E102 [29,30]. The dye can be found as a coloring agent in ice creams, sweets, chewing gum, jelly, custard powder, etc. [30]. Moreover, it is used in the pharmaceutical industry as a coloring agent for shells of gelatin capsules [30]. Despite the broad applications of tartrazine dyes in food and pharmaceutical industries, the World Health Organization (WHO) has classified the dye as a toxic chemical. The World Health Organization (WHO) has set a maximum daily tartrazine intake of 0–10 $mgkg^{-1}$ of body weight [29]. Studies revealed that consuming tartrazine through contaminated food or water can cause multiple diseases, such as thyroid cancer, asthma, and migraines [28–30]. The carcinogenic nature of tartrazine dye is influenced by the tendency to interact with protein structure [29].

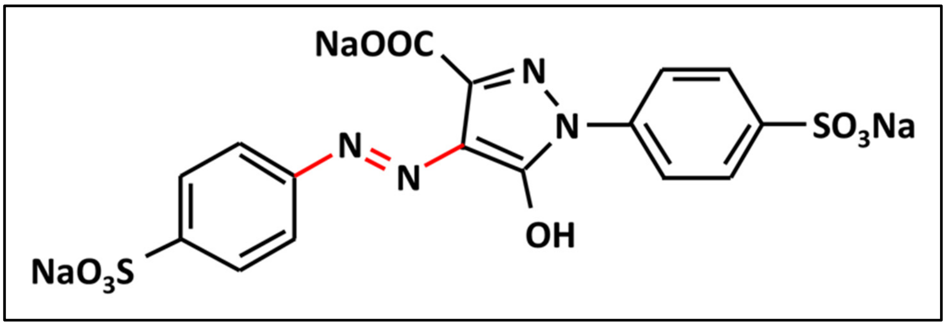

Figure 6. The chemical structure of Tartrazine azo dye.

Congo Red and Disperse Red 1 are two red azo dyes used widely in the textile industry (Figure 7). Like other dyes, wastewater contaminated with Congo Red or Disperse Red 1 is typically discharged directly into the environment. The health and environmental impacts of Congo Red and Disperse Red 1 are covered by multiple studies. Fernandes et al. have conducted an extensive study on the effects of Disperse Red 1 on reproductive health [31]. They exposed sexually mature male mice to small dosages of Disperse Red 1 through forced feeding. Subsequently, they tracked the health performance of the mice for specific periods between 8.3 and 24.9 days. The data revealed a dramatic reduction in mouse fertility. The obtained data showed a direct relationship between the consumption of Disperse Red 1 and the detection of testicular diseases. Additionally, the consumption of Disperse Red 1 dye is associated with the detection of DNA damage in mice and *Salmonella spp.* [25,31]. In further studies, Congo Red has shown a similar toxicity effect on mouse health. In fact, Congo Red affected the reproductive system of both male and female mice [31].

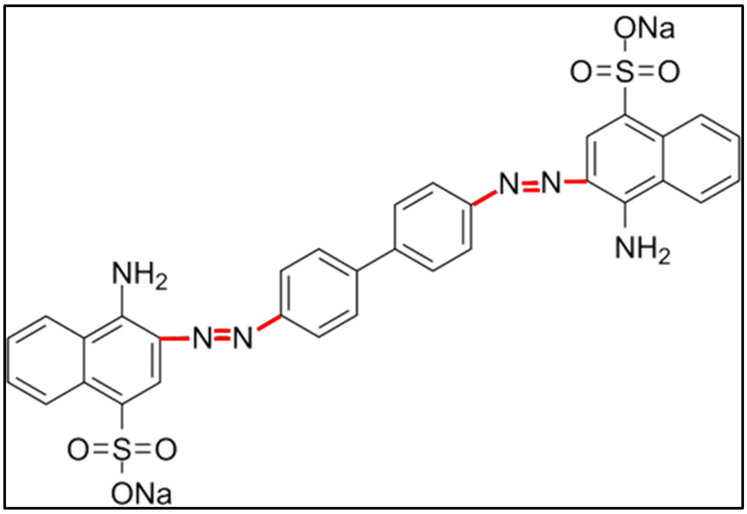

Figure 7. The chemical structure of Congo Red azo dye.

Sudan dyes are classes of lipophilic azo dyes that produce colors in the range of yellow, orange, and red [25]. Sudan dyes are extremely harmful to human health and cause carcinogenic and teratogenic effects [25,32]. Several countries in the European Union have banned the use of Sudan dyes [32]. Moreover, Japan and the United States have suspended using Sudan dyes in many applications [32]. Despite the strict regulations on monitoring the use of Sudan dyes in many countries, several industries have continued using the dyes illegally as coloring agents for food and textile dying. Sudan dyes and their derivatives are used in spice mixtures, sauces, paprika powder, chili powders, etc. [25,32]. The family of Sudan dyes includes Sudan I, II, III, IV, Sudan Orange B, Sudan Red G, Sudan Red 7B, and Sudan Black B (Figures 8 and 9) [25,32]. Sudan, I dye, also known as Solvent Yellow, is among the most widely adopted dyes in the food industry [25]. The toxicity associated with Sudan dyes is related to the diffusion of metabolic substances such as aniline and 1-amino-2-napthol in human and animal bodies. Compared to other types of azo dyes, the chemical structure of Sudan dyes is affected by the action of intestinal flora, therefore releasing metabolic substances within the digestive system [25,32]. Studies show that consuming Sudan dyes through contaminated water or food may cause spleen and bladder tumors [25,32]. The health impact of azo dyes on mice is illustrated by Figure 10. Despite the strict banning of Sudan dyes in the European Union, 20 medical cases are reported annually associated with consuming imported products containing the dyes [32].

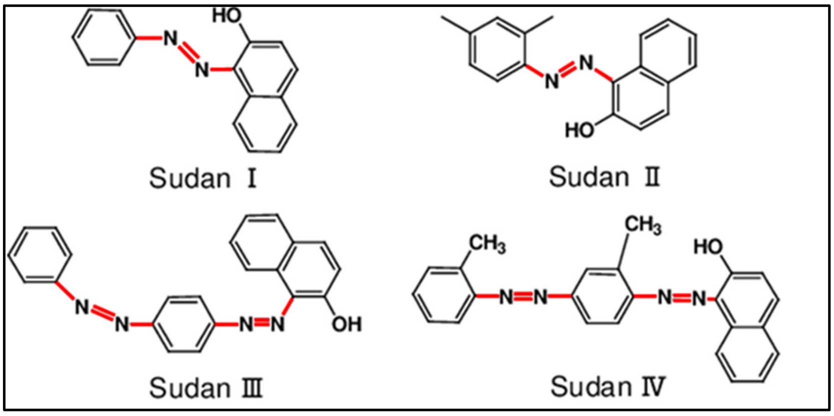

Figure 8. Chemical structure of Sudan I, II, III, IV.

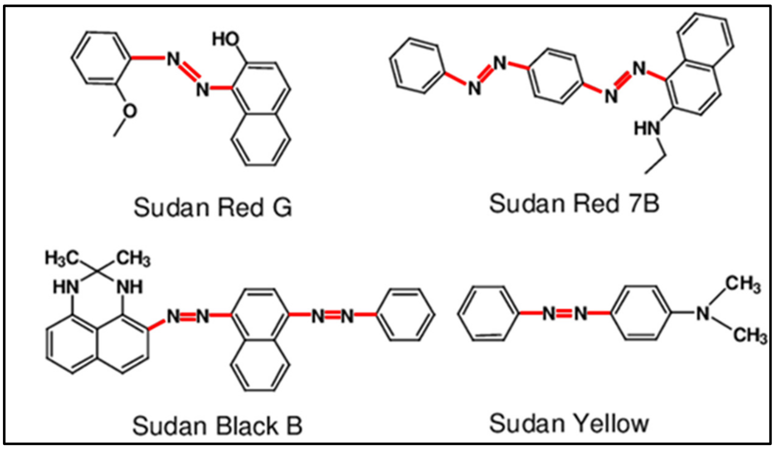

Figure 9. Chemical structures of Sudan Red G, Sudan Red 6B, Sudan Black, and Sudan Yellow.

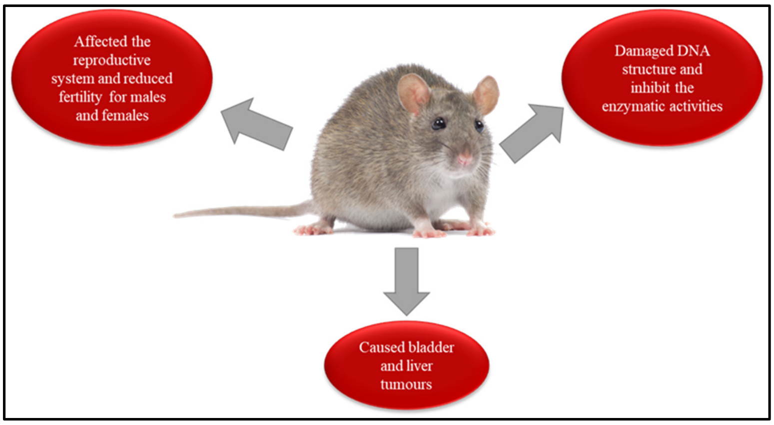

Figure 10. The reported health impacts of azo dyes on mice.

Several chemical and physical methods have been studied to eliminate the azo dyes discharged into the environment. Some of these methods include ion-exchange, chemical precipitation, coagulation and flocculation, reverse osmosis, membrane filtration, biological degradation, and adsorption [2,30]. The primary objective of these studies is to develop a highly efficient azo dye removal technique at a low cost. Despite its simplicity, the adsorption methodology has shown the best performance in removing several types of azo dyes from contaminated water compared to other methods [30]. Due to its unique physicochemical properties, activated carbon is used as an adsorbent to remove the azo dye. From an economic perspective, the preparation costs of activated carbon are lower than other adsorbents, such as metal oxides or biosorbents. Nevertheless, conducting more studies on activated carbon is crucial as it cannot be efficient for absorbing every type of azo dye. The modification of activated carbon properties relies on several factors, such as the type of precursor used in the synthesis process and the type of activation agent. This paper reviews multiple studies conducted on preparing activated carbon for azo dye removal. Additionally, the methodology adopted for preparing activated carbon is covered to compare the efficiency of removing the azo dyes from contaminated water.

3. Treatments Methods for Dye-Contaminated Effluents

A thorough understanding of the techniques and design of any process for removal of azo dyes is essential. There are multiple techniques applied for contaminant removal from water/wastewater. These techniques cover all stages of the water/wastewater treatment plant, including initial, primary, secondary, and tertiary treatment [33]. The development of each stage is influenced by the increase in demand for high-quality water. To illustrate, some urban cities and industries treat water to the secondary or even more advanced stage. According to Rajasulochana and Preethy, the development of water treatment techniques is affected by different factors, such as the cost of the process, types of contaminants and their concentration in water, the heterogeneity of discharged pollutants, and the required level of purity [34]. Hence, it is impossible to treat most of the contaminants in a single stage [34]. In general, this overview covers the techniques used in the advanced stages to remove dyes from wastewater. The data obtained from the sources of dyes help to categorize the contaminates associated with water pollution, hence using suitable techniques in the removal process [33]. The water treatment technologies used in dye removal are classified into two types: physicochemical and biological treatment processes [1,5,6,35]. The physicochemical processes involve technologies such as membrane filtration (separation), ion exchange, reverse osmosis, chemical precipitation, coagulation and flocculation, electrochemical treatment, photocatalytic, and adsorption [36]. The treatment techniques can be combined to form hybrid water treatment techniques. Usually, hybrid techniques have more removal efficiency and can solve environmental problems handled by using conventional techniques.

3.1. Coagulation and Flocculation

Many water treatment plants use coagulation and flocculation as water clarification techniques. Historically, coagulation and flocculation have been used to supply clean water (sweet water) [37–39]. However, coagulation is used for water clarification and not for water purification due to the lack of knowledge about germs and waterborne diseases [37–39]. Coagulation and flocculation must be distinguished from the precipitation process. Basically, the coagulation process is the removal of non-settleable minute particles from an aqueous solution by neutralizing the solution [39]. Usually, coagulation is used to remove colloidal impurities. The addition of coagulants such as alum neutralizes the solution, and then particles flocculate together, forming micro flocs [39]. Moreover, chemicals such as polymers are added to enhance the flocculation and form larger particles known as macro flocs [38,39]. In simple words, the basic principle behind coagulation and flocculation is the accumulation of microparticles to form settleable or floatable macro particles. The agglomerated particles are removed from water via sedimentation and filtration. Figure 11 illustrates the steps of the coagulation and flocculation process.

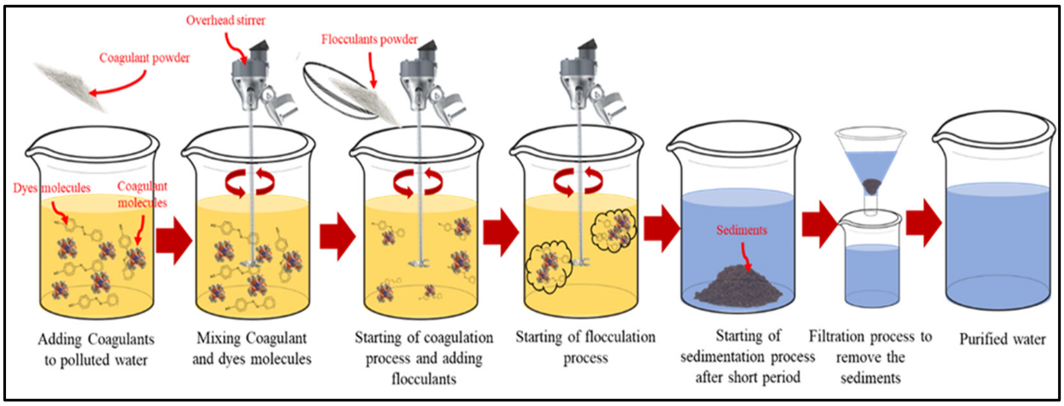

Figure 11. Schematic of Coagulation–Flocculation for textile dye wastewater treatment.

Although coagulation and flocculation are the most used treatment methods, the removal performance of the methods is low compared to other techniques [39]. The efficiency of coagulation is influenced by different factors such as the type and dosage of coagulants/flocculants, stirring speed and time, temperature and settling time, retention time (RT), and pH level of the solution [39–41]. The properties of applied coagulants are the vital factor in determining the coagulation efficiency [39,41]. Some of the coagulants used in the water treatment field are magnesium, iron derivatives, lime, and aluminum salt. According to Mathuram et al., ferrous sulphate, ferric chloride, and ferric chloride sulphate showed high efficiency as coagulants in removing several types of dye [42]. Typically, coagulation is mixed with other water treatment techniques such as electrochemical processes and adsorption to enhance the treatment efficiency [43]. Electrocoagulation involves the use of metal electrodes submerged in polluted water. The electrodes dissolve metal ions which adsorb the dye molecules and precipitate to form sediments (Figure 12) [44,45]. Furthermore, magnesium carbonate and hydrated lime are utilized to adsorb azo dyes and form coagulants [46,47].

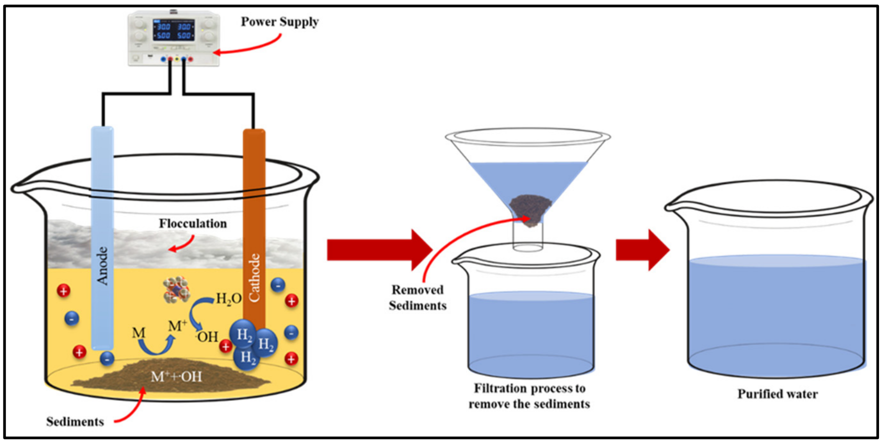

Figure 12. Schematic of electrocoagulation for textile dye wastewater.

Wang et al., published an interesting study on the application of the coagulation process for removing different types of azo dyes from water [48]. They used cucurbituril for coagulation and targeted three different azo dyes, Congo Red, acid red 1, and orange II [8]. The obtained results demonstrated the tendency of the coagulants to remove Congo Red and acid red 1. The reported removal rate for these dyes was above 95% under pH 6.

Furthermore, the result showed that the removal percentage is influenced by pH, contact time, and the structure of the dyes [48].

Even though chemical coagulants have several advantages in terms of cost and simplicity, they produce a significant amount of toxic contaminants and impurities. Moreover, the process can be costly in the case of adopting electrocoagulation, as it consumes high electricity [44]. Thus, there is a crucial need to develop non-toxic, highly efficient coagulants to eliminate the presence of toxic substances in water.

3.2. Photocatalytic Degradation

Photocatalysis is an advanced abiotic oxidation method used to remove contaminants from wastewater. Indeed, the photocatalysis process is preferred over other techniques due to its unique advantages, such as eliminating contaminants under harsh conditions in a short time [49]. Studies have revealed that photocatalysis is highly efficient for removing endocrine-disrupting chemicals (EDCs) from water [12]. The process is conducted under light radiation where photocatalyst and electron–holes pairs form. The photocatalyst formation and the electron–holes pairs are associated with the degradation of pollutants in water [12] (Figure 13).

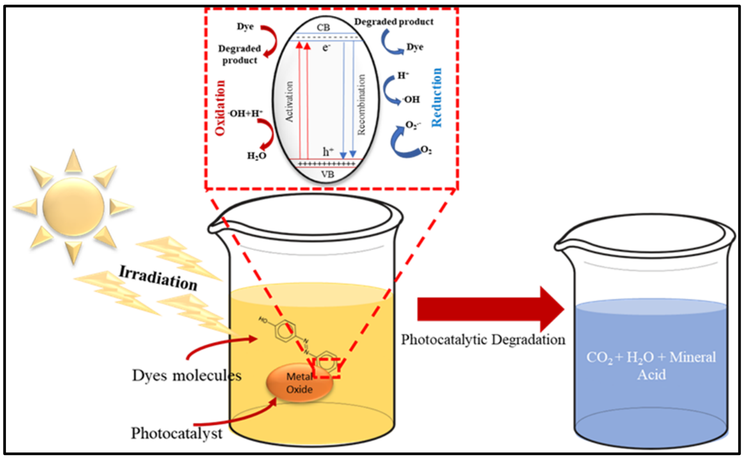

Figure 13. Schematic of Photocatalytic Degradation of toxic dye.

There are several types of photocatalyst used in water treatment, such as titanium dioxide (TiO_2), iron (Fe), zinc oxide (ZnO), and copper oxide (CuO). TiO_2 is highly popular among other photocatalysts as it has high efficiency in degrading different organic contaminants. In addition, TiO_2 is inexpensive and environmentally friendly. Nonetheless, photocatalytic degradation has multiple disadvantages that limit the scope of its applications. For instance, the photocatalytic process is considered costly for large-scale applications. Moreover, the operation of the photocatalytic process is extremely difficult as the process is pH dependent. Photocatalysts have the tendency to form an aggregation of nanomaterials; therefore, it is usually combined with other chemicals and techniques. Although the process is considered eco-friendly to some extent, the process produces highly toxic byproducts.

Mabuea et al., performed research on photocatalyst applications for azo dye degradation [50]. The study covered the use of the transition metal carbides molybdenum and tungsten, along with a multiwalled carbon nanotube (MWCNT) for the photocatalytic degradation process. Molybdenum and tungsten were coated with transition metals like iron (Fe), cobalt (Co), and nickel (Ni), which enhances the decomposition performance. The transition metal carbides were used for Congo Red azo dye degradation under sunlight irradiation [50]. The process was repeated in the dark where no photocatalytic reaction is initiated, and under the light but in the absence of a photocatalyst. The results revealed that the MWCNT doped with Ni and Co had the highest decomposition efficiency, which was 97.1%. The results demonstrated that the performance of the photocatalytic process is better compared to photolysis for decomposing Congo Red azo dye [50].

3.3. Ion Exchange

Ion exchange is a form of sorption process used widely for water treatment to reduce the level of ionic chemical species and hardness of water. Basically, ion exchange is a process in which two ions with similar charges are interchanged between two electrolytes or electrolyte particles and complex [51]. The ion exchange process is influenced by the coulombic attraction [51]. In the water treatment field, the ion exchange process is used for decontamination, separation, and purification [51,52]. Typically, the ion exchange technique is combined with other techniques such as membrane separation, coagulation and flocculation, and adsorption to improve the removal efficiency. The synthetic compounds used as ion exchangers are known as resins. These compounds are solid, insoluble, and contain weakly bonded ions on the surface. When ions in the solution pass through the exchange resin, the ion exchange process occurs between ions on the resin surface and ions in the solution [51,53]. The process continues until the ion exchange reaches equilibrium. However, when equilibrium is established, and resins are saturated, backwashing is applied to regenerate the resins and remove accumulated ions and contaminants [53]. The ion exchange process can be explained using the following formula:

$$A^{+}B^{-} + X^{+} + Y^{-} \text{->} X^{+}B^{-} + A^{+} + Y^{-} \tag{1}$$

where A^{+} is the exchangeable ion on the ion exchanger, and X^{+} and Y^{-} are ions in the aqueous solution. Ion exchange resins are classified into two types: gel and porous resins. Gel resins have the cross-linked structure of a polymer. The polymer is connected in the form of a matrix and has different functional groups uniformly distributed among the structure [51–53]. The unique structure of the polymer helps in increasing the volume of ions attached to the functional groups. These functional groups work as ion active sites where the exchange process occurs. The increased volume of the diffused ions means more ions in the solution will attach with the large number of active sites on the resin. Porous resins have pore surfaces where ions can attach easily. The porosity of porous resin varies according to the size of the structure. Porous resins can be microporous, mesoporous, and macroporous. The size of the resin affects the surface area, hence affecting the ion exchange capacity of the resin. A higher surface area means more ions diffuse and are attached to the resin.

Different cationic and anionic resins are used to remove ionic dyes, such as methylene blue, methyl orange, and malachite green [54]. However, the removal efficiency of the ion exchangers relies on several factors, such as the concentration of the dyes in the targeted aqueous solution, and the amount of the ion exchangers. Basically, the removal percentage of ionic dyes from contaminated water increases with decreased concentration of dye and increased amount of resin. Recently, anionic ion exchangers have been used widely to remove azo dyes from wastewater [54]. Although the ion exchange process has shown great performance in eliminating different types of pollutants from water, it is considered a very expensive process. Moreover, the ion exchange process produces highly toxic sludges that need to be carefully discharged. Additionally, ion exchange has time-consuming and costly operational processes. Thus, the adsorption process and membrane filtration are combined with ion exchange to eliminate some of the limitations of the technique and to increase the removal performance.

3.4. Electrochemical Technique

The electrochemical method has shown promising results in many fields and applications, such as batteries, sensors, soil treatment, and fuel cell technology. In general, electrochemical techniques have been used in water and wastewater treatment to eliminate water contaminants [55]. The concept of using electrochemical techniques for water remediation revolves around applying an electrical current to start a chemical reaction to generate new substances. Usually, electrochemical techniques are used in combination with other water treatment techniques, such as coagulation, flotation, adsorption, and membrane filtration. Some of the most popular techniques used for dye removal are electrocoagulation, electrochemical reduction, indirect electro-oxidation, photo-assisted electrochemical, and electrodialysis [7,33,53,55,56]. As a result of the variety of electrochemical methods available today, we can change the controlling parameters independently to improve the effectiveness of treatment. In other words, electrochemical treatment of dye-contaminated water needs a minimum amount of energy.

Generally, electrochemical oxidation of dye-contaminated water is conducted via either direct anodic oxidation, or chemical reaction. In direct anodic oxidation, the reaction occurs during the oxidation and reduction processes. Indeed, direct anodic oxidation has inefficient decontamination performance. On the other hand, a chemical reaction occurs during the generation of electro-species [55]. Typically, during the chemical reaction, some of the organic dyes transform into biodegradable composites such as carboxylic acids, or totally oxidize into CO_2 and inorganic ions [55]. Although electrochemical techniques have high removal efficiency for dye particles, they are considered extremely expensive techniques and usually require pre-treatment of the contaminated effluents.

3.5. Membrane Filtration

A wide variety of membrane technologies have been used extensively in the field of water treatment. It is true that membrane technologies have demonstrated significant growth in the field of water treatment compared to other methods of treatment. The attention drawn toward membrane technologies is driven by the fact that it requires low energy, low-to-no chemical usage, and inexpensive operational cost [57,58]. Therefore, it is considered environmentally friendly, with some limitations. The limitations of membrane technologies are caused by membrane fouling with toxic sludge production.

Generally, based on chemical structure, membrane technologies can be classified into two types: organic and inorganic membranes. Furthermore, the membrane can also be classified as isotropic and anisotropic membranes. Primarily, isotropic membranes are uniformly composed membranes with poor porous structure. Whereas an anisotropic membrane is composed of a non-uniformed structure with multiple layers [57,59]. Organic membranes consist mainly of organic polymers and can have different pore sizes. On the other hand, inorganic membranes are synthesized from materials such as metals, silica, and ceramics. Membranes can be further classified based on the size of the pores into macro membranes, micromembranes, and nanomembranes, which all contribute to multiple processes such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis.

For dye removal, nanofiltration and reverse osmosis are considered the most efficient types of membrane techniques. This is due to the proper nano size of the pores in the membrane, which catch the azo dye particles more efficiently compared to ultra- or microfiltration techniques. It has been found that a membrane with a weight cut-off lower than 10,000 Daltons is suitable for eliminating dye molecules from water [12,40]. Although membrane filtration is considered a cost-efficient technique for removing contaminants from water, there are some limitations that restrict its application up to a certain extent. For instance, the membrane process is affected by the flow rate of the medium and requires scheduled cleaning to remove the concentrated waste. Moreover, membrane filtration has poor contaminant removal efficiency compared to other techniques [57,58]. Nonetheless, membrane filtration techniques are usually used with other methods such as electrochemical, adsorption, or ion exchange as hybrid techniques. Membrane hybrid techniques are considered more reliable and efficient as they reduce the limitations of the water treatment methods.

3.6. Electrodialysis Process

Electrodialysis is an advanced hybrid treatment method used in several wastewater treatment plants around the world. In fact, electrodialysis is one of the great examples of hybrid treatment methods in the water treatment field. Basically, electrodialysis is a combination of electrochemical and ion exchange methods [56]. Primarily, the electrodialysis method is used for the desalination of brackish water to remove salt. Additionally, it has been used as a removal process for heavy metal ions and ionic dyes [55,56]. In electrodialysis, the electric potential generated via the electrochemical process is used to drive electrolyte ions through a series of selective ion exchange membranes. Hence, the electric potential is considered as a driving force of the process [55]. The selectivity and the chemical structure of the ion exchange membranes in the electrodialysis method are like the ion exchange resins [55,56]. However, the difference can be observed in the mechanical requirement of the membrane process. The simple structure of the electrodialysis cell consists of two conductive electrodes separated via two ion exchange membranes. The separation of the membranes divides the electrodialysis cell into three compartments where chemical reactions occur. When a direct current (DC) is applied to the electrodialysis cell, cations and anions in the solution start to move towards their perspective electrodes (cathode and anode). During the transportation of the cations and anions, they pass through ion exchange membranes that help in ion removal and separate the compartment of the electrodialysis cell by ions volume [56]. The concentration of ionic contaminants decreased in the middle compartment. However, the concentration is higher close to the anode and cathode sides. During the process, cations can only pass through a cation exchange membrane, while anions pass thought an anion exchange membrane. Usually, the electrodialysis method involves a formation of acid and alkaline layers near the anode and cathode, respectively. As a result, additional hydrogen and hydroxide ions move to the middle compartment. In the middle compartment, hydrogen and hydroxide ions neutralize and form water. Selective ion exchange membranes are used to reduce the negative effect of the movement of hydrogen and hydroxide ions and hence increase the current efficiency.

3.7. Biodegradation Techniques

In the last few decades, the adoptability of biodegradation techniques for water treatment has increased dramatically. The rapid development in biodegradation techniques is mainly driven by the special characteristics of the techniques, such as the low operational cost, high removal efficiency, and the generation of a reduced amount of toxic byproduct [60]. Biodegradation techniques are used for the degradation or elimination of chemicals such as heavy metals, azo dyes, microplastics, and organic toxicants. Moreover, in some contaminated areas, microorganisms are found to be living on digesting dyes as a source of carbon and nitrogen [12]. Nevertheless, the consumption of discharged dyes by microbial communities in the affected areas has a negative impact on the environment. The uncontrolled consumption of dyes by microbial communities can affect the ecosystem via increasing the population of the microbes which will eventually destroy the ecosystem [61]. For instance, Krishnamoorthy et al. conducted a study on the impact of discharged azo dyes on the abundance of *Saccharibacteria* [2]. The study was conducted on the Noyyal River in Tamil Nadu, India. Typically, textile industries around the Noyyal river discharge a huge amount of contaminated textile wastewater that contains a high concentration of azo dyes. The presence of azo dyes in the river resulted in a higher population of Saccharibacteria and Proteobacteria. Consequently, the ecosystem of the river is becoming unstable. Moreover, Saccharibacteria has a negative impact on human health as it is associated with oral mucosal infectious diseases [28].

Generally, biodegradation for dye remediation can be carried out using fungi, bacteria, algae and plants, and yeasts. The efficiency of the microorganism is determined by its natural activity and availability [62]. The biodegradation of the azo dyes is mainly influenced by the used cell or enzymes. However, the degradation process can also involve the use of microbial biomass, which is more efficient in eliminating the toxic dyes [62]. The biodegradation process decomposes the dye particles completely. However, it is a time-consuming process and is often not efficient for a large volume of contaminated water.

3.8. Adsorption

The importance of the adsorption method in the water treatment field is crucial. IN particular, the adsorption method is involved with other treatment methods such as precipitation, coagulation, and ion exchange to treat industrial wastewater and groundwater. Basically, adsorption in water treatment is a process used to remove dissolved contaminants via adhering them to a surface of solid particles [63]. In other words, adsorption is a process of diffusing and adhering atoms, molecules, or ions onto the surface of solid particles. The adhesion of the particles occurs due to the existence of imbalanced forces between the solid surface and the contaminated particles [63]. The solid surface that attracts molecules is known as an absorbent, and the particles which are adsorbed are known as adsorbates. The adsorption process can be illustrated by the following formula, where A is adsorbate, B is adsorbent, and AB is the output when A is adsorbed by B:

$$A + B \leftrightarrow AB \tag{2}$$

The adsorption method is preferable due to its simplicity and flexibility. In fact, operations using the adsorption process are very simple compared to other treatment methods. Adsorbents are added directly to the water sources or by mixing basins. In addition, the adsorption treatment process is safe, cheap, and can be used to remove various types of contaminants (organic, inorganic, and biological) [7,33,63]. The special characteristics of the adsorption method are affected by several factors such as the aqueous solution properties, type of adsorbate, adsorbent type, structure of the pollutant, operating conditions, contaminant disposal, and particle regeneration [63,64].

In general, there are two types of adsorption: chemical adsorption—chemisorption—and physical adsorption—physisorption [63,65]. Basically, chemical adsorption is defined as the adhesion of particles to the solid surface via chemical bonds such as ionic, covalent, or metallic bonds [63]. In contrast, physical adsorption involves the adhesion of particles to a solid surface via physical bonds such as the van der Waals force [63]. Physical adsorption differs significantly from chemical adsorption in terms of their bond strength.

In order to develop the optimum adsorbent, a full understanding of the method and the behavior of the interaction between adsorbents and adsorbates is mandatory. Lately, attention has been drawn toward using activated carbon to treat textile dye wastewater. Activated carbon has various advantages and is considered in multiple applications due to its unique features (Table 2).

Table 2. Advantages and disadvantages of some dye elimination techniques.

Technique	Advantages	Disadvantages
Coagulation and flocculation	-Inexpensive. -Simple operation procedures.	-Produces huge amount of toxic sludge. -Poor efficiency. -Requires long operation time.
Photocatalytic degradation	-Highly efficient. -Can be used under harsh conditions.	-Extremely expensive. -Produces highly toxic byproducts.
Adsorption	-High removal efficiency. -Inexpensive. -Simple operation procedures.	-Requires treatment for adsorbents. -Not efficient with all types of dye.
Ion exchange	-Inexpensive. -Produce small amount of byproduct.	-Not efficient with all types of dye. -Requires long time.
Membrane filtration	-Efficient with all types of dyes. -Requires short time.	-Expensive process. -Produces a high volume of toxic sludge.

3.9. Application of Activated Carbon for Dye Removal from Wastewater

Activated carbon, also known as activated charcoal, is a carbonaceous material composed of many open pores on the surface (Figure 14). Activated carbon is used in many applications, like the automotive field, to filter the interior air of the vehicle, in gasoline tanks to eliminate the amount of discharged toxic substances, and as electrodes for the batteries and electrochemical capacitors [66]. Activated carbon is part of the graphite family, and therefore it is amorphous in nature. Activated carbon has remarkable properties, such as a unique pore structure, high surface area, and chemical polarity. These properties depend on the type of the precursor and the preparation process [67–69]. The enlarged surface area and porous texture are formed via exposing turbostratic carbon to different chemical reactions (Figure 14) [69]. The chemical reaction interacts with the surface molecules of activated carbon and produces gases. Consequently, gases escape from the surface and create pores. The chemical reaction involved in activated carbon preparation is known as activation.

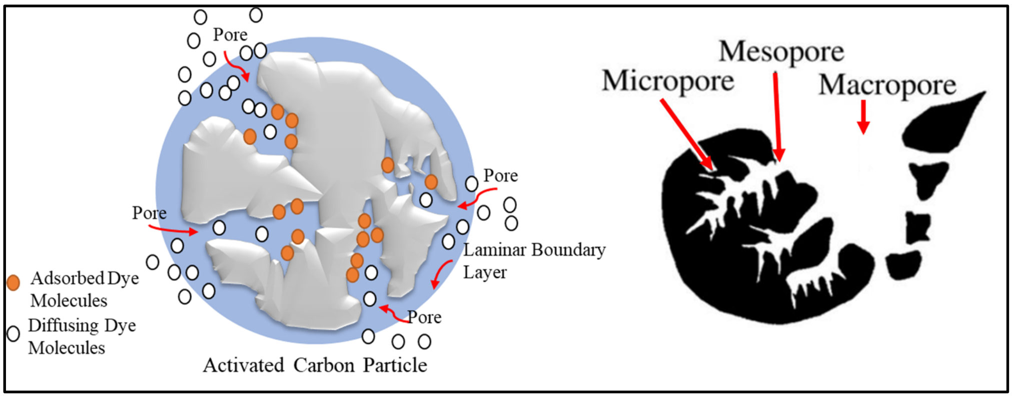

Figure 14. Pore structure and distribution on activated carbon.

In recent decades, commercial activated carbon has been used for multiple applications. However, commercial activated carbon is not cost-effective because it is produced from non-renewable sources such as coal and petroleum. Thus, efforts are geared towards using eco-friendly, renewable, and, most importantly, inexpensive sources of precursors for producing activated carbon. Biomass precursors have been introduced as a highly effective alternative. As a result, biomass based on agricultural wastes is used to synthesize new forms of activated carbons [69]. There are many types of agricultural wastes that can be used as precursors for activated carbons. For instance, palm kernel shells, waste coffee beans, cassava peel waste, rice husk, sugarcane bagasse, olive husk, hazelnut shells, almond shells, walnut shells, and many more [66,67,69].

The type of the precursor influences the properties of the produced activated carbon, such as the surface area, porosity, and particle size [69]. Activated carbon is classified according to particle size into three types, Powdered Activated Carbon (PAC), Granular Activated Carbon (GAC), and Activated Carbon Fibers (ACF) [66]. Activated carbon is categorized by particle size because it is difficult to distinguish its physical properties and surface characteristics [66]. PAC has a particle size between 0.015–0.025 mm, whereas GAC and ACF have a particle size between 0.6–3 mm and 10–20 µm, respectively [66] (Table 3). PACs and GACs are usually used in the water treatment field, whereas ACFs are used for gas adsorption due to their special microporous structure.

Table 3. Comparison between PACs, GAC, and ACFs.

Activated Carbon	**Particle Size**	**BET Surface Area (m^2/g)**	**Pore Volume (cm^3/g)**	**Physical Surface Area (m^2/g)**
PACs	0.015–0.25 mm	700–1600	0.5–1.4	-
GACs	0.6–3 mm	700–1500	0.5–1.1	~0.001
ACFs	10–20 μm	700–2500	-	0.2–2.0
Activated carbon	Particle size	BET surface area (m^2/g)	Pore volume (cm^3/g)	Physical surface area (m^2/g)
PACs	0.015–0.25 mm	700–1600	0.5–1.4	-
GACs	0.6–3 mm	700–1500	0.5–1.1	~0.001
ACFs	10–20 μm	700–2500	-	0.2–2.0

Generally, PAC is best for batch adsorption, whereas GAC is best for the column adsorption process used industrially. Nonetheless, PAC is typically used to establish the process kinetics and isotherms initially, then based on the harder nature of the starting biomass containing more lignin, the industry prepares GAC particles. Because softer, cellulosic biomass such as leaves, and grass are not utilized to produce granular activated carbon. ACF fibers are generally great for small-scale applications as they will have more weight loss, like PAC.

The interaction between the particles of toxic dye as an adsorbate and activated carbon as an adsorbent is mainly influenced by several possible adsorption mechanisms. Initially, the interaction between the adsorbent and adsorbate begins with the surface and intra-particle diffusion processes. Then, several adsorbing mechanisms may occur at the surface of the adsorbent, such as π–π interactions, hydrogen interactions, acid–base reactions, electrostatic interactions, hydrophobic interactions, and van der Waals forces [69]. Typically, electrostatic attraction and ion exchange are the most common adsorption mechanisms of dyes using activated carbon [69]. The adsorption mechanisms are mainly influenced by the functional groups on the surface of the activated carbon and ions in the dye solution. Thus, modification of the activated carbon surface will enhance the reactivity and promote adsorption of more dye particles. Usually, multiple adsorption mechanisms occur simultaneously during the adsorption process. Figure 15 shows an example of possible mechanisms of dye adsorption.

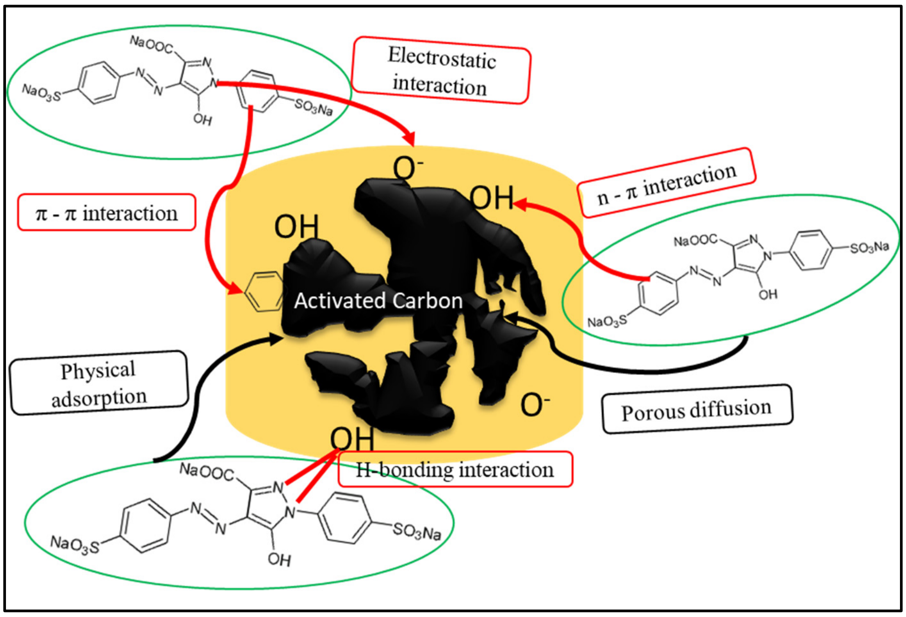

Figure 15. Possible mechanisms for adsorbing dyes onto activated carbon.

Synthesis of activated carbons involves two stages, thermochemical carbonization, and activation [69]. These two stages can occur simultaneously, one-step process, or sequentially, two-steps process. The thermochemical carbonization stage is conducted either via hydrothermal process, pyrolysis, torrefaction, or combustion [69]. However, the activation stage involves physical, chemical, or physiochemical activation [66]. Generally, the carbonization process occurs in an inert atmosphere where oxygen is absent to prevent biomass burning. Nevertheless, combustion occurs with oxygen to reduce energy content in biomass [66,67]. The temperature required for the carbonization process is in the range of 200–400 °C, while for pyrolysis and hydrothermal it is between 400–850 °C and 200–350 °C, respectively [66,69].

The product obtained from the thermochemical carbonization processes is known as char. Indeed, char is considered an adsorbent, but it has poor adsorptive capacity. Thus, different chemical reagents, such as acids or bases, are used to activate the surface of the char and produce activated carbon. This process is known as chemical activation. Usually, acids such as phosphoric, sulfuric, and hydrochloric acids are used in the activation process [69]. The main goal of using chemical activation is to enhance the number and size of pores on the surface of the carbon. Hence, it can catch more of the dye particles. The adsorption capacity varies with the type of activation reagent used. Physical and chemical activations are the most used methods in preparing activated carbon [69]. While the physiochemical activation method combines both physical and chemical activation, it is often used to enhance the adsorption performance for specific applications. Generally, activation processes are used to improve the porosity of the activated carbon particles. The generated pores are classified into macropores (>50 nm), mesopores (2–50 nm), and micropores (<2 nm) [66]. Figure 16 shows the adsorption process of dyes molecules using activated carbon.

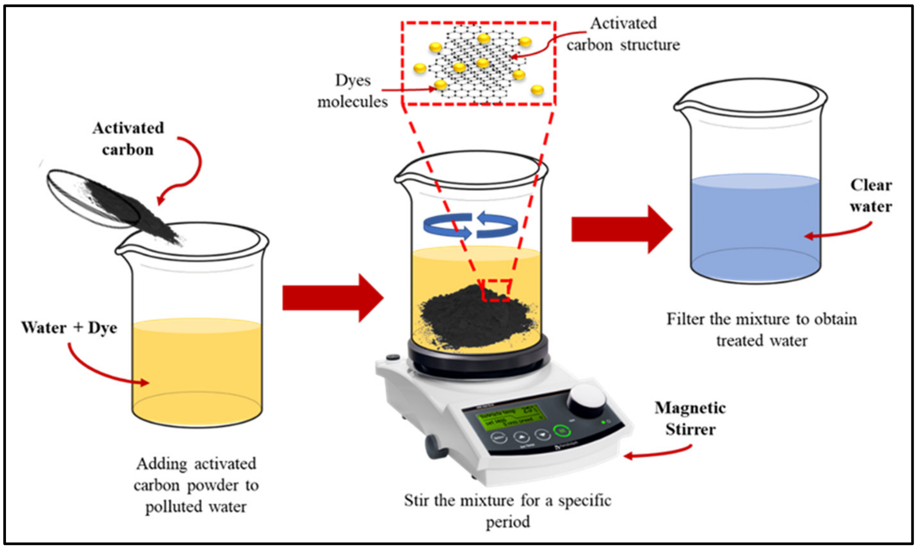

Figure 16. Adsorption mechanism of activated carbon for dyes particles.

3.9.1. Renewable Bio-Based Precursors for Synthesis of Activated Carbon

Synthesizing activated carbon through renewable precursors revolves around the adoptability of different types of lignocellulosic biomass. Lignocellulosic biomass is an abundant natural material. Historically, lignocellulosic biomass has been used as a source of energy. Although the efficiency of biomass as a source of energy is lower than fossil fuel, lignocellulosic biomass is an environmentally friendly and affordable substance [69]. Additionally, lignocellulosic biomass substances are used to produce value-added products such as fertilizers and activated carbon.

In general, lignocellulosic biomass structure is composed of three biomacromolecules: cellulose, lignin, and hemicellulose. The complex structure of lignocellulosic biomass requires a higher amount of energy (temperature and pressure) for carbonization and activation [66,67]. The percentage of each type of biomacromolecule varies based on the different types of lignocellulosic substances. Pyrolyzing lignocellulosic biomass with a high percentage of cellulose and hemicellulose will result in producing liquids and gases. The treated liquids and gases are known as biofuel and biogas. On the other hand, pyrolyzing lignocellulosic substance with high amount of lignin will produce solids in the form of biochar, which is the precursor of activated carbon [69]. Generally, carbonization of lignocellulosic biomass will produce biomaterials with ashes. Basically, the produced ashes are the minerals that are part of the lignocellulosic biomass structure.

Cellulose

Cellulose is considered one of the core compounds in many organic structures. Cellulose is an abundant compound and is simple to extract from lignocellulosic biomass. The chemical structure of cellulose consists of six carbon glucose units connected in the form of a linear polymer [70]. Additionally, the structure of cellulose contains two terminals with different activities. The first terminal is known as the reducing end group, and it consists of the reducing hemiacetal group in position C1 [70]. The second terminal is known as the non-reducing group and consists of an extra secondary hydroxyl group in position C4. The carbon glucose units in the cellulose structure are linked together via β-(1-4)-glycosides bonds, where cellulose polymers are structured together parallelly [70–72]. Generally, cellulose has poor solubility in several types of solutions due to the interconnection between the glucose units and cellulose polymers. The interconnection of cellulose is affected by the existence of intermolecular and intramolecular hydrogen bonds [70]. The percentage of cellulose in biomass material varies according to the characteristic of the biomass. Typically, biomass materials with a high percentage of cellulose are used to obtain organic fuel in the form of biofuel. The process of producing biofuel involves thermochemical conversion processes at low-to-medium temperatures.

Hemicellulose

Hemicelluloses are heteropolymers that are present in the plant cell wall structure along with cellulose. Hemicelluloses have random amorphous structures that are composed of multiple monosaccharide units linked together [73,74]. Thus, hemicellulose is considered a polysaccharide with β-(1-4)-linked backbones. The primary role of hemicellulose is to form a bond with cellulose and lignin to strengthen the plant cell wall. The hemicellulose class includes xyloglucans, xylenes, mannans and glucomannans, and β-(1→3,1→4)-glucans [73]. The core of the hemicellulose structure is pentose sugar. In contrast to cellulose, the hemicellulose structure consists of random short chains. Therefore, hemicellulose's solubility is better than that of cellulose [70]. The polymers in hemicellulose are classified into heteropolymers and homopolymers. The difference between the polymer classes revolve around the type of sugar units [73]. The heteropolymers consist of several types of sugar units, whereas homopolymer units are composed of a single type of sugar. Like cellulose, hemicellulose is also used to produce bio-products such as biogases and biofuel.

Lignin

Lignin is a complex cross-linked polymer present in the structure of lignocellulosic biomass materials. The primary role of lignin is to provide strength to the lignocellulosic biomass materials [75]. In general, lignin's structure consists of different phenyl propane units and aromatic alcohol. Moreover, hydroxyl groups and methoxyl groups are present in the lignin structure and are usually targeted to form other materials [69]. Hydroxyl groups exist in the para position, whereas methoxyl groups exist in meta positions. Additionally, the aromatic rings in the structure are linked together via carbon-to-carbon or carbon-to-oxygen bonds. The structure of lignin is composed of multiple functional groups such as carbonyl, hydroxyl, and methoxyl groups that influence the physiochemical properties of the material [75,76]. For instance, the presence of these groups makes the structure of lignin strong and insoluble. The percentage of lignin in the lignocellulosic biomass materials varies, depending on the type of biomass material. Approximately, the structure of biomass may consist of 10% to 30% lignin. However, the structure of materials like coconut fibers and husk may be 45% lignin, whereas hardwood contains 16% to 24% lignin, and softwood is composed of 25% to 31%. Besides the volume of lignin in the biomass, the structure of the lignin also can vary between the different types of lignocellulosic biomass materials [69,75]. To illustrate, lignin in hardwood relates to xylenes via a covalent bond, whereas softwood is connected to galactoglucommannans, which is hemicellulose [75,76]. Lignocellulosic biomass with a high percentage of lignin is used to produce carbonaceous solids such as char and activated carbon. Hence, the quality and structure of the biomass has a significant impact on the properties of synthesized activated carbon used for wastewater treatment.

3.9.2. Synthesis Protocol of Activated Carbon

Physical Activation Process

Physical activation involves the oxidation of char using water steam (H_2O), diluted oxygen gas (DO), carbon dioxide (CO_2), and many other oxidization agents [66]. Usually, physical activation is conducted at a temperature up to 1100 °C [77]. The most remarkable oxidizing agent is carbon dioxide. Carbon dioxide is endothermic and has low reactivity at high temperatures, forming enormous pores on the activated carbon structure [78]. Moreover, controlling the activation process using carbon dioxide is less complicated and inexpensive. Carbon dioxide, as an activation agent, tends to form more micropores, whereas water steam tends to expand the existing micropores. Consequently, water steam generates activated carbons with low micropore volume and high meso- and macropore volume [78]. Nonetheless, both carbon dioxide and steam can be very effective activating agents, as the conditions of the activation process can also alter the pore structure of the activated carbon [78]. The properties of water steam and carbon dioxide can be suitable for certain types of biomass precursors with low lignin percentages [69]. The physical activation process is commercially favorable, as it is inexpensive and requires no chemicals. Therefore, the process is considered environmentally friendly. On the other hand, physical activation has drawbacks that limit its scalability, such as the production of activated carbon with low adsorption capacity, consumption of high energy, and long activation period [77]. It is essential to carefully select a suitable oxidizing agent for the used precursor to obtain activated carbon with large pore size distribution and surface area.

Chemical Activation Process

The chemical activation process, known as wet oxidation, uses chemical agents to dehydrate and oxidize charcoal. These activating agents can be acids, bases, or salts. Usually, the activation process is synchronized with the carbonization process at a temperature between 400 and 900 °C, according to the type of precursor used and activating agents [77]. The chemical activation process is divided into three main stages. First is the impregnation stage, in which the biochar is oxidized and dehydrated with chemicals. Subsequently, the mixture is dried and then heated for a given period under a specific temperature. Lastly, the mixture is washed repeatedly to remove the excess activating agent to obtain activated carbon [77]. Although several chemicals have been studied as activating agents, only a few can produce activated carbon with high efficiency. The activating agents with high potential are either alkaline or acidic groups. Examples of commonly used alkaline groups are sodium hydroxide (NaOH), potassium carbonate (K_2CO_3), potassium hydroxide (KOH), and calcium chloride ($CaCl_2$). On the other hand, the most used acidic groups are sulphuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) [79–81]. In addition to acid and alkaline groups, some metal salts have revealed a high potential, such as zinc chloride ($ZnCl_2$) [77]. Typically, potassium hydroxide produces activated carbon with a high surface area, though this is also associated with the type of used precursors [66,77]. Certain variables need to be monitored to obtain activated carbon with a high pore size and volume, such as activation method, carbonization temperature and time, and impregnation ratio [77].

Among the various types of chemical activators, H_3PO_4 has been used widely in the large-scale manufacturing of activated carbon [81]. The intensive use of H_3PO_4 in the commercial production of activated carbon is mainly influenced by several factors, such as low environmental impact, low energy consumption, high carbon yield, and ease of recovery [12]. Ernawati et al. documented the effect of phosphoric acid (H_3PO_4), salt (NaCl), and potassium hydroxide (KOH) as activation agents [13]. The study focused on the impact of the activation agents on the preparation of activated carbon from Tanjung fruit peel. The results revealed that activated carbon produced using H_3PO_4 as an acidic activation agent has high porosity and hence greater adsorption performance compared to NaCl and KOH [13]. Generally, H_3PO_4 influences the structure of the activated carbon via two methods. Primarily, H_3PO_4 initiates hydrolysis, condensation, and dehydration reactions by acting as a catalyst. Secondly, H_3PO_4 may occupy some micropores on the interior structure of activated carbon and expand the surface area due to the size of the particles [12]. Hence, phosphoric acid can be utilized to produce activated carbon to target specific types of contaminants.

Although chemical activation produces activated carbons with more pore size distribution and high pore volume, the process has drawbacks that limit its applicability. For instance, producing activated carbon via chemical activation requires repeated and long washing steps to remove the excess activating agent [69]. Moreover, the process produces toxic wastewater containing some chemical agents that can harm the environment if discharged inappropriately [77]. Nonetheless, chemical activation has several advantages that make it desirable over physical activation. For instance, chemical activation produces activated carbon with high adsorption capacity. Moreover, the process is economically viable because it requires lower temperature and less activation time [77]. Table 4 summarizes the list of adsorbents used to remove dyes from wastewater.

Table 4. List of some adsorbents used for the removal of dyes from wastewater.

Adsorbent	**Dye**	**Removal Capacity**	**pH**	**Ref.**
Activated carbon	Tartrazine	24.57 mgg^{-1}	2	[9]
Pulp ash and paper sludge	Reactive Blue 19	95%	12	[82]
Metal hydroxide sludge	Direct Blue 85	98.7 mgg^{-1}	10	[83]
Red mud	Remazol Brilliant Blue	~72%	2	[84]
Activated red mud	Acid blue 113	83.33 mgg^{-1}	3	[85]
Activated red mud	Reactive black 5	35.58 mgg^{-1}	3	[85]

Physiochemical Activation Process

In the last decade, the development of the industrial sectors increased rapidly, and hence new types of complex materials and toxic wastes have been introduced into the environment. As a result, a crucial need for more efficient removal methods arose which led to more studies in the water treatment field. Despite the application of activated carbon for water treatment, studies have tried to enhance the adsorption performance by applying new techniques and synthesizing new composites. Physiochemical activation is a process that combines both chemical and physical activation to obtain activated carbon with a high pore volume and a large surface area. Generally, physiochemical activation is achieved via one of two approaches. The first approach involves pre-chemical treatment of biomass materials before carbonization, followed by physical activation. In the second approach, the biomass material is carbonized and then treated using chemical and physical activations (Table 5). The sequence of the physiochemical treatment has a negligible impact on the performance of the produced activated carbon. The activated carbon obtained through physiochemical activation has a better pore structure compared to chemical or physical activation. However, the activation process is considered costly and time-consuming.

Table 5. Chemical, Physical, and Physiochemical activation of different types of biomass materials.

Precursor	Activation Method	Activation Agent	Activation Temperature (°C)	Activation Time (Minutes)	S_{BET} (m^2/g)	Adsorption Capacity (ppm)	Pore Volume (cm^3/g)	Reference
Barley straw	Physical activation	CO_2	800	60	789	-	0.3268	[86]
Barley straw	Physical activation	Water steam	700	60	552	-	0.2304	[86]
Palm oil shell	Chemical activation	Na_2CO_3	700	120	743.71	247.33	0.4210	[87]
Palm oil shell	Chemical activation	$ZnCl_2$	700	120	551.05	241.67	0.3137	[87]
Green coconut shell	Chemical activation	$ZnCl_2$	650	60	995.79	-	0.372	[88]
Date stone	Physical activation	CO_2	900	120	604	28,570	0.29	[89]
Rice husk	Chemical activation	KOH	800	180	1505	-	0.42	[90]
Sour cherry stones	Physio-chemical activation	$ZnCl_2$ with CO_2 steam	700	120	1704	-	0.984	[91]
Olive stones	Chemical activation	H_3PO_4	500	120	1218	-	0.5	[92]
Olive stones	Physical activation	Water steam	750	360	807	131,000	0.30	[93]
Garlic peel	Chemical activation	KOH	800	60	1262	-	0.65	[94]
Rice straw	Chemical activation	KOH	850	120	1048.3	-	0.0436	[95]
Tea waste	Physical activation	Water steam	800	30	995.07	-	0.287	[96]
Date seeds	Physio-chemical activation	HNO_3/Steam	-	180	950	-	-	[97]

3.9.3. Activated Carbon for the Elimination of Azo Dyes

Reviewing previous studies on removing azo dyes via activated carbon will help to find the optimum parameters of the adsorption process. Several approaches have been published on the application of different techniques and materials for dye elimination [98–103]. As an eco-friendly and inexpensive material, activated carbon has demonstrated a persistent market demand. There are various parameters that can be modified to create the optimum adsorbents for certain types of azo dyes. Most of the studies on removing azo dyes from the water via activated carbon have focused on the effect of the activation agent type.

Researchers have studied removing tartrazine and sunset yellow azo dyes from contaminated water using activated carbon derived from cassava sievate [100]. In their study, they used phosphoric acid (H_3PO_4) as an activation agent [100,103]. The reported optimal removal of the dyes was 20.83 mgg^{-1} and 0.091 mgg^{-1} for tartrazine and sunset yellow, respectively. The results were recorded at optimum conditions at a temperature between 30–40 °C, adsorbent dosage equal to 0.1 g, and pH in the range of 1–2. Typically, tartrazine and sunset yellow removal from contaminated water is conducted simultaneously due to the similarity between the two dyes in the structural formula [100].

Earlier research was conducted on the removal of tartrazine from contaminated water using activated carbon prepared from apricot stone biomass impregnated with phosphoric acid (H_3PO_4) [101]. Their study involved two approaches: a batch adsorption experiment and a fixed-bed column experiment. In their study, they found that the most effective parameters in the batch experiment were initial dye concentration and temperature. Moreover, the optimum adsorption capacity was reported at 76 mgg^{-1} after two hours. According to their report, higher dye concentration resulted in higher adsorption capacity. Furthermore, the temperature had a significant influence on the adsorption capacity; the higher the temperature, the higher the adsorption capacity.

An interesting study published by Brice et al., 2021, studied the elimination of tartrazine from an aqueous solution using activated carbon powder [9]. The activated carbon was produced from cola nutshell and chemically activated via phosphoric acid (H_3PO_4) and potassium hydroxide (KOH). They conducted the adsorption experiment using both chemical agents under different parameters. The study focused on the effect of adsorbent dosage, contact time, and type of the activation agent. The pH level was fixed at 2 because the adsorption performance was extremely weak under pH lower than 2. The characterization results showed that the obtained activated carbons had a mesoporous structure with multiple oxygen functional groups on the surface. The adsorptivity of both potassium hydroxide-based activated carbon and phosphoric acid-based activated carbon increased with the increase in contact time. The reported adsorption capacity was 18.196 mgg^{-1} and 19.256 mgg^{-1} for potassium-hydroxide- and phosphoric-acid-based activated carbons, respectively. The study of adsorption isotherms is described by the Langmuir model, where the maximum monolayer adsorption capacity was 21.5 mgg^{-1} and 24.5 mgg^{-1} for potassium-hydroxide- and phosphoric-acid-based activate carbons [9].

Kumar et al., 2013 published a study on removing Direct Blue 5 azo dye using commercial granular activated carbon [101]. According to the study, Direct Blue 5 is used intensively for textile dying in Sanganer, India. The research focused on studying the impact of retention time, initial concentration of the dye, and stirring time. The analytical results revealed that granular activated carbon has a high tendency toward adsorbing Direct Blue 5 azo dye. Additionally, the maximum monolayer adsorption capacity was found to be 17.5 mgg^{-1}.

Rajaram and Patil used activated carbon for the removal of Sudan Red G azo dye from a contaminated aqueous solution [33]. The activated carbon was prepared from two different types of precursors, mosambi peel and cotton stems. The adsorbent was activated using sodium bicarbonate ($NaHCO_3$). The research examined the effects of several parameters, including adsorbent dosage, initial concentration of dye, contact time, and pH. The results revealed that the adsorption capacity increased with the increase in contact time and adsorbent dosage. The maximum removal percentage was 92.73%, reported after 120 min of contact time and at an adsorbent dosage equal to 1 g/100 mL [33].

Li et al., 2016, conducted a study on the usage of activated carbon as an adsorbent for several types of dyes [102]. The published study included an azo dye known as methyl orange. The activated carbon was synthesized from rice husk residue and activated using sodium hydroxide (NaOH) and phosphoric acid (H_3PO_4) in two steps. Like other studies, they investigated the effects of pH, contact time, temperature, and initial concentration of the dye. The results showed that the maximum amount of removal of methyl orange took place at pH 3. Moreover, the adsorption capacity of the activated carbon decreased with the increase in pH above 3. Similarly, the increase in the initial concentration of the dye resulted in a decreased removal rate of methyl orange [102].

A recently published study by El Maguana et al. 2020 removed methyl orange azo dye using activated carbon produced from prickly pear seed cake [104]. The synthesis process of activated carbon involved using phosphoric acid (H_3PO_4) as an activation agent. This study revealed that the activated carbon produced had an excellent adsorption performance. The maximum adsorption capacity was found to be 336.12 mgg^{-1} at pH 7 and temperature 20 °C.

Liu and Xing, 2021, studied the adsorption process of acid red 88 azo dye from contaminated water using activated carbon as an adsorbent [105]. The activated carbon was prepared from the carbonization of pomelo peels and sodium hydroxide (NaOH) activation. The study was conducted based on an orthogonal experiment to enhance the removal capacity of the activated carbon. Several factors were studied in order to optimize the adsorption performance. These factors included activation time, temperature, the activation agent type, and impregnation ratio. The characterization results showed that the structure of obtained activated carbon was amorphous and composed of micropores. The maximum adsorption capacity was found to be 1473.59 mgg^{-1}. The adsorption capacity was mainly influenced by activation temperature and impregnation ratio.

Sidiqua and Priya, 2021, conducted an interesting study on removing basic yellow azo dye from contaminated wastewater using activated carbon composite [106]. The activated carbon was prepared from sapindus seed using sulfuric acid activation. The obtained activated carbon was mixed with clay to form the composite adsorbent. The contact time and pH were used as controlling variables in the adsorption experiment. The results demonstrated that the composite adsorbent had a higher adsorption capacity compared to pure activated carbon and clay. The reported removal percentage of composite adsorbent was 86% at maximum contact time, whereas the removal percentages of activated carbon and clay were 68.5% and 38%, respectively. The analytical results revealed that the increase in contact time assists the absorbent and enhances the removal percentage drastically [36].

4. Conclusions

It is without a doubt that azo dyes can have serious consequences for humans and the animals surrounding the ecosystem when they are released directly into the environment. Azo dyes are used widely in several industries, such as the textile, food, wood, paper, cosmetic, and pharmaceutical industries. Hence, humans can be exposed to toxic dyes through different channels. Typically, short-term exposure to some azo dyes does not show serious health risks. The long-term exposure to azo dyes, regardless of whether they are ingested or breathed in, can result in a few carcinogenic and mutagenic diseases. Therefore, different water treatment techniques are studied to eliminate the pollutants from natural water resources. Numerous studies have been conducted on the removal of toxic azo dyes from discharged wastewater using an adsorption process. The majority of these studies have been conducted using activated carbon synthesized from locally available biomass materials. As presented in this work, activated carbon performance on adsorbing azo dyes varies according to several factors. These factors include the type of biomass, activation agent, pH, activation temperature, contact time, initial concentration of dye, adsorbent dosage, etc. The potential of activated carbon as an adsorbent for azo dyes is very high. There can be a great deal of research conducted on optimizing the absorptivity of activated carbon for the absorption of specific types of azo dyes in the future.

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