Sustainable Adsorbents from Plant-Derived Agricultural Wastes for Anionic Dye Removal: A Review

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Abstract: The extensive use of dyes in numerous industries results in massive dye discharge in the wastewater, which is a major cause of water pollution. Globally, the consumption of dyes is near seven hundred thousand tons across different sectors, of which around 10–15% goes into the wastewater. Among the dye kinds, anionic dyes make up the main proportion, having a 32–90% share in the wastewater. Different plant-derived wastes, which are sustainable given their natural abundance, effectiveness, and low cost, are frequently proposed for dye separation. However, these adsorbents are inherently more suitable for cationic dyes than anionic dyes. In recent years, the modification of these wastes has been progressively considered to suit them to anionic dye removal. These modifications involve mechanical, thermal, or chemical treatments, or combinations. These attempts propose two-way benefits, as one abundant waste is being used to cure another severe problem, and eventually both could be diminished. This review has a key focus on the evaluation of plant-derived adsorbents and their modifications, and particularly for anionic dye adsorption. Overall, the mechanism of adsorption and the suitability of the current methods are discussed, and their future potential is explored.

Keywords: lignocellulose; natural biomass; dye wastewater; adsorption isotherm; Congo Red; diffusion and kinetics

1. Introduction

Dyes are comprehensively used in food, pharmaceutical, textile, plastic, metal, and many other manufacturing industries to impart the colors of choice to the end products. Currently, more than seven hundred thousand tons of dyes are required each year across different sectors, of which at least 10–15% are discarded into the wastewater [1]. Although the use of dyes is unavoidable, it is also responsible for massive water pollution, which is a major concern. Anionic dyes are the known main fraction (nearly 32–90%), compared with all other dye kinds (such as cationic or nonionic dye), in the wastewater. These include the acid, direct, reactive, and soluble forms of some nonionic dyes, which are difficult to eliminate due to their high solubility in water [2]. These dyes not only alter the color of water, but they also inhibit light penetration and reduce the rate of photosynthesis and the oxygen level, causing damage to the entire aquatic ecosystem [2]. Often, these dyes are carcinogenic and initiate various diseases in humans, such as the dysfunction of the kidneys, reproductive system, liver, brain, and central nervous system, and they bring hazards to other living organisms [3]. Therefore, it is essential to remove these dyes from wastewater to attain a sustainable environment. In the recent past, there has been a growing interest in the removal of anionic dyes from wastewater, and particularly in the last few years. For instance, a search of the keyword ‘anionic dye removal’ in the Web of Science database (title, abstract, keywords only) recalled 4981 articles starting from 1975 (this number is 3637 from...
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Several techniques are proposed for removing anionic dyes from wastewater, such as physical (membrane filtration, ion exchange, irradiation, coagulation), chemical (oxidation, ozonation, photochemical, electrochemical destruction), and biological (aerobic and anaerobic microbial degradation) treatments [4]. However, the adsorption method is still a preferred method of dye removal due to its simplicity and efficiency [5]. There is an ongoing interest in preparing more sustainable adsorbents from agricultural and other natural plant-derived wastes, as they are widely available at a low cost. These resources are chemically known as lignocellulose, and they are often collectible at a negligible cost. The composition of lignocellulose biomasses (such as wheat straw, rice straw, oat straw, bagasse, cotton gin trash, and so on) is mostly cellulose (40–50%), intimately associated with hemicellulose (20–30%) and lignin (10–25%) [6]. However, due to their chemical nature, they are more prone to adsorb cationic dyes than anionic dyes. This is because the lignocellulose structure is chemically composed of different anions as its active sites, such as the hydroxyl and carbonyl groups, and it generally shows a negative surface charge [7]. Thus, it is important to modify them to take advantage of their abundance and utilize them for anionic dye separation. Over the years, several modification methods of these wastes have been proposed, including combinations of mechanical, thermal, or chemical treatments, to enhance the adsorption ability of these resources.

Because the use of agricultural wastes for dye separation is a massive area of research and the interest is increasing, currently, there are several reviews available that summarize these findings. However, these are mostly based on all classes of dyes [4,8–10], rather than with any particular focus on the anionic dye class. Due to the natural attraction of cationic dyes to the lignocellulosic structure, the removal of cationic dyes has received more interest compared with the removal of anionic dyes, which limits the discussions for the anionic dye adsorption in reviews in which both classes are discussed. However, as mentioned above, anionic dyes are the major proportion of all other dyes, and the separation of these dyes needs specific attention. The adsorption of anionic dyes is essential, but more challenging, compared with cationic dyes. In recent years, numerous common lignocellulosic wastes, such as rice husk [11], wheat straw [12], sawdust [13], cotton waste [7], banana waste [14],...
corn stalks [15], orange peel [16], eucalyptus bark [17], coffee waste [18], and many other resources, have been proposed for the successful separation of anionic dyes, showing the variety and possibility of these raw materials for anionic dye removal. Therefore, this review aims to evaluate the findings reported for anionic dye adsorption from plant-derived agricultural wastes, and to explore the suitability of the proposed methods and reveal their future potential.

2. Types of Anionic Dyes

Based on their ionic nature, dyes can be classified into two categories: ionic and nonionic (Figure 2). Anionic dyes are a type of ionic dye in which anions are the key active groups. Some nonionic dyes, such as vat and disperse dyes, need to be converted into soluble anionic forms before being applied on a substrate [7]. Anionic dyes can be classified into reactive, direct, and acid dyes based on their application process.

Historically, the chemistry of dyes and pigments has mostly been studied in the context of textile materials, as the coloration of textiles demands that extensive quality parameters be met, which are not relevant to other industries. Understanding their mechanism of interaction with fibers (such as cellulose) can also provide an indication of their interaction ability when adsorbents from agricultural wastes are used for dye removal, as the chemical nature of these wastes is also mostly cellulosic or lignocellulosic.

2.1. Reactive Dye

Reactive dyes can form a covalent bond with certain fiber active sites, such as the hydroxyl group (-OH) or amino group (-NH$_2$) [19]. Lignocellulosic biomasses contain plenty of hydroxyl groups around their structures, thus making them accessible to interact with reactive dyes. Commercial reactive dyes commonly contain the dichlorotriazine, trichloropyrimidine, aminochloro-s-triazine, sulphatoethylsulphone, dichloroquinoxaline, aminofluoro-s-triazine, and difluorochloropyrimide groups [20]. Because reactive dyes and the surface of cellulosic fibers become negatively charged in water, electrolytes (such as sodium chloride or Glauber salt) are often used to neutralize the fiber surface. No matter how reactive the chemical groups of these dyes are, it is hard to achieve over 80% dye fixation in actual dyeing, which causes the obvious discharge of unfixed dyes as hazardous effluent [21].
2.2. Direct Dye

Direct dyes are named from their high affinity towards cellulosic fiber, and they are thus said to be directly applicable onto cellulose-based fiber systems during dyeing. The major chromophores in the structure of direct dyes are the azo, anthraquinoid, phthalocyanine, and metal complexes [19]. These dyes are highly substantive, although not reactive. The use of electrolytes is also required for the successful attachment of direct dyes to cellulosic fibers.

2.3. Acid Dye

Acid dyes have acidic groups in their structures and are mainly applied on noncellulosic fibers, such as protein and polyamides in acidic conditions. The chromophoric systems in acid dyes are sulphonated azo, anthraquinone, nitrodiphenylamine, triphenylmethane, and xanthenes [22]. Cationized fibers can produce a bond with an anion of acid dyes through an electrostatic force [23].

3. Chemical Nature of Plant-Derived Agricultural Wastes

Common plant-based agricultural wastes are a complex combination of cellulose, hemicellulose, and lignin, and are thus also widely known as lignocellulosic biomass. As shown in Figure 3, these constituents are complexly attached in the lignocellulosic structure. Cellulose is the major component that is linearly formed from the D-glucose subunits, and it is commonly known for its higher crystallinity [24]. However, the hemicellulose part (such as pentose and hexose) is randomly oriented within cellulose chains and is known to impact negatively on the crystallinity. Their chain length is much shorter than the typical chain length of cellulose. The other part, lignin, is the outer layer that holds together both cellulose and hemicellulose [25]. It is a complex structure of cross-linked phenolic subunits, although its actual structure is still to be identified [26]. Throughout the lignocellulosic structure, there are abundant hydroxyl groups, which make this material highly hydrophilic and ideal for dye adsorption from water. For the same reason, their surface is electronegative, and they attract cationic dyes more as the cations of dye become easily attached to the anionic hydroxyl groups. Therefore, their properties need to be altered for efficient anionic dye removal, which has frequently been attempted by researchers over the years.

![Figure 3. Common chemical groups in plant-derived agricultural waste.](image)

4. Adsorbents for Anionic Dyes

As mentioned above, due to the electronegative nature of the surface of agricultural wastes (i.e., lignocellulosic structure), anionic dyes show a repulsive effect during the attachment through ionic interactions, if the adsorbent surface is not modified [7]. The
 modification of these materials can be divided into three main broad concepts: (1) mechanical, (2) chemical, and (3) thermal modifications. The concept of mechanical modification is mainly to reduce the particle size of the initial material by cutting or mechanical milling [27]. This may involve some chemical treatment (e.g., for cleaning purposes), but it will not necessarily alter the chemical groups or ionic behavior. However, the principle of the second concept (i.e., chemical modification) is exactly the opposite, where the modification of the chemical groups is performed to make them chemically more interactive with anionic dyes [16]. This method may involve mechanical milling as a preliminary step, although chemical treatments are the main driving factor for the dye adsorption. The other concept is thermal modification, where both mechanical milling and chemical treatment may be present, although the main principle is to convert the biomass into a carbonaceous material (such as activated carbon) by high-temperature carbonization processes [28], which often result in a high surface area, which leads to the key improvement in the adsorption property. All three methods are promising from different aspects and have their benefits and drawbacks.

4.1. Mechanical Modifications

The mechanical modification of biomass mainly involves the mechanical-milling operation, where the materials are crushed into fine or coarse powder (Figure 4 and Table 1). Although the chemical properties are not altered, the adsorption capacity largely depends on bath conditions and is often found as a complex synergistic influence from many parameters. Although anionic dyes have a general repulsive effect on the lignocellulosic surface, at the initial stage, the dye adsorption largely depends on the force generated by the dye-concentration gradient from the solution [29]. At the beginning of adsorption, this force helps the dye molecules to reach the adsorbent surface, overcoming the repulsive effect. However, after a certain level, when the concentration gradient is reduced by some of the dyes adsorbed onto the adsorbent, the repulsive effect starts to take the active role and limits the adsorption rate. Hence, even with a similar surface area, mechanically modified biomass can often adsorb more cationic dyes than anionic dyes [30]. This indicates that there is the possibility of remaining vacant sites inside the adsorbent (not completely saturated), even when the equilibrium is reached.

![Figure 4. Schematic of the key concept of the mechanical modification of plant-derived agricultural waste for anionic dye removal.](image-url)
Table 1. Maximum adsorption capacities ($q_{max}$) of anionic dye adsorbents derived from mechanically modified agricultural wastes.

| Resources                          | Particle Size (µm) | Dye                     | $q_{max}$ (mg/g) | Reference |
|-----------------------------------|--------------------|-------------------------|------------------|-----------|
| Waste tea residue                 | 0.3475             | Acid Blue 25            | 127.14           | [31]      |
| Date stones and jujube shells     | 50–100             | Congo Red               | 45.08–59.55      | [32]      |
| Waste banana pith                | >53                | Direct Red              | 5.92             | [33]      |
| Waste banana pith                | >53                | Acid Brilliant Blue     | 4.42             | [33]      |
| Jujuba seeds                     | 53–150             | Congo Red               | 55.56            | [34]      |
| Cotton plant wastes              | 75–500             | Remazol Black B         | 35.7–50.9        | [35]      |
| Lotus                            | <100               | Congo Red               | 0.783–1.179      | [36]      |
| Almond shell                     | 100–500            | Eriochrome Black T      | 123.92           | [37]      |
| Waste of corn silk               | 250–500            | Reactive Blue 19        | 71.6             | [27]      |
| Waste of corn silk               | 250–500            | Reactive Red 218        | 63.3             | [27]      |
| Banana peel, cucumber peel, and potato peel | 250–500           | Orange G                | 20.9–40.5        | [30]      |
| Eucalyptus bark                  | 250–700            | Solar Red BA            | 43.5             | [17]      |
| Eucalyptus bark                  | 250–700            | Solar Brittle Blue A    | 49               | [17]      |
| Saccharomyces cerevisiae (yeast)  | 315–400            | Acid Red 14             | 18–23            | [38]      |
| Mushroom waste                   | <400               | Direct Red 5B           | 18               | [39]      |
| Mushroom waste                   | <400               | Direct Black 22         | 15.46            | [39]      |
| Mushroom waste                   | <400               | Direct Black 71         | 20.19            | [39]      |
| Mushroom waste                   | <400               | Reactive Black 5        | 14.62            | [39]      |
| Ash seed                         | ≤1000              | Cibacron Blue           | 67.114           | [40]      |
| Bean peel                        | ≤1000              | Cibacron Blue           | 28.490           | [41]      |
| Jute processing waste            | 10,000             | Congo Red               | 13.18            | [39,42]   |
| Corn stigmata                    | Ground (size not mentioned) | Indigo Carmine    | 63.7             | [39,43]   |
| Cotton gin trash                 | Film form           | Acid Blue 25            | 35.46            | [7]       |

It is almost a rule of thumb that a smaller-size particle possesses more surface area, and hence, it can hold a greater amount of dye. This has been found to be true in countless studies, and it has been proven for anionic dye adsorption as well. For example, the adsorption capacity of eucalyptus bark towards Solar Red BA (a direct dye) was below 10 mg/g when a particle size of 0.51–0.71 mm was used, although it reached 18.15 mg/g when a <0.255 mm size was used [17]. A similar observation was also found in another report in which the adsorption of Eriochrome Black T was significantly improved (~22.8%) when the particle size of an almond-shell adsorbent was reduced from >500 µm to <100 µm [37].

4.2. Chemical Modifications

Due to the poor interaction of lignocellulosic biomass with anionic dyes [1], the chemical modification of their surface has received keen attention. In most cases, the main idea was to bring cationic groups to the surface, which facilitated the dye adsorption. Several methods of achieving the cationized adsorbent are reported in varied dimensions. As shown in Figure 5, these can be divided into four main categories: treatment with amine-based chemicals, cationic surfactants, quaternary ammonium compounds, and acid solutions.
Different amine-rich compounds have mostly been chosen by researchers for the chemical modification of lignocellulosic biomass because they contain a high number of amines that easily become attached to lignocellulose and attract anionic dyes. However, these methods often require multiple steps of chemical treatment to effectively modify the structure. For instance, Wong et al. used polyethylenimine to treat coffee waste for the adsorption of reactive and acid dye [18]. The method included the impregnation of coffee-waste powder in a polyethylenimine solution at a moderate temperature (65 °C) for 6 h, and then cross-linking using glutaraldehyde. This delivered 77.5 mg/g and 34.4 mg/g maximum adsorptions of Reactive Black 5 and Congo Red dyes, respectively. Nevertheless, a comparison with the unmodified coffee waste was not reported to validate the true influence of the cationization. In another study, nanocrystalline cellulose extracted from hardwood bleached pulp was amino-functionalized by ethylenediamine [44]. The process involved the treatment of ethylenediamine at 30 °C for 6 h, and an in situ reduction by NaBH₄ at room temperature for 3 h, which resulted in the 553.6 mg/g maximum adsorption of Acid Red GR, although no comparison was shown with unmodified lignocellulose. In a different study, wheat straw was treated with epichlorohydrin and N,N-dimethylformamide at 85 °C for 1 h. Furthermore, an ethylenediamine treatment (45 min at 8 °C) and trimethylamine treatments (120 min at 85 °C) were applied to achieve the final amino-modified wheat-straw powder, which showed maximum adsorption capacities of 714.3 mg/g for anionic dye (Acid Red 73) and 285.7 mg/g for reactive dye (Reactive Red 24) [12].

Coating with amine-based polymer was also performed, where sawdust coated with polyaniline nanofibers removed up to 212.97 mg/g of Acid Red G [45]. These nanofibers were prepared by the polymerization of an aniline monomer and oxidant (FeCl₃). The inclusion of polyaniline nanofibers enhanced the surface area of the biomass (from 1.22 to 16.26 m²/g), which was useful for the adsorption. In one study, an amine-rich biopolymer, (chitosan) was used to modify lignocellulose for anionic dye adsorption [7]. The chitosan was dissolved in an acetic acid solution, and the cotton-gin-trash film was impregnated for 1 h at room temperature. The resultant modified adsorbent showed a significant increase in the adsorption capacity of Acid Blue 25 (151.5 mg/g) compared with that of the unmodified biomass (35.5 mg/g). The amine-based adsorbent was also prepared as a form of a nanocomposite. For instance, banana-peel cellulose was combined with chitosan and silver nanoparticles to investigate its suitability to adsorb Reactive Orange 5, reaching a maximum adsorption capacity of 125 mg/g [14].
In the second category, treatment with cationic surfactants commonly increases the aliphatic carbon content in biomass [15], but most importantly, they induce the cationic groups on the surface, which help anionic dye removal. Several studies have been performed to modify lignocellulosic biomass using different cationic surfactants. These include cetylpyridinium bromide [15], hexadecylpyridinium bromide [46,47], hexadecylpyridinium chloride [48], hexadecylpyridinium chloride monohydrate [49], cetyltrimethylammonium bromide [50], and hexadecyltrimethylammonium bromide [51]. This technique commonly involves the continuous shaking of the crushed lignocellulose particles in the surfactant solutions, and mostly at room temperature. However, the maximum adsorption achieved through this technique is somewhat lower than the amine-based methods. For example, a few of the adsorption capacities reported for this method are 70 mg/g dye by modified wheat straw [47], 30.8–31.1 mg/g dye by modified corn stalks [15], 55–89 mg/g dye by modified coir pith [51], and 146.2 ± 2.4 mg/g dye by modified orange-peel powder [16], which are comparatively lower than most of those reported for amine-based modifications (Table 3). This is probably related to the abundance of amide groups [18] in the amine-based compounds, which are more prone to attach to the lignocellulosic structure, as well as with the anionic dyes, by electrostatic attraction [7,18].

There are few studies on the modification of lignocellulose by quaternary ammonium compounds for anionic dye adsorption, which mostly showed high efficiency. For example, Jiang and Hu reported hydroxypropylctadecyldimethylammonium-modified rice husk cellulose for reactive (Diamine Green B) and acid-dye (Congo Red and Acid Black 24) adsorption. This modification required multiple steps, which included alkaline and ultrasonic treatments, and treatments with epichlorohydrin and N,N-dimethyl-1-octadecylamine/isopropanol. The resultant adsorbent was able to adsorb up to ~580 mg/g of the anionic dye (Congo Red) [52]. In another study, biomass from palm kernel shell was quaternized using N-(3-chloro-2-hydroxypropyl)trimethylammonium chloride in an alkaline aqueous mixture, which resulted in 207.5 mg/g of maximum adsorption [53].

The fourth category of the chemical modification of the lignocellulose surface is through acidic treatment. For instance, it was claimed that a phosphoric acid treatment worked by increasing the surface area and led to the grafting of phosphate onto the lignocellulose structure. However, the adsorption capacity reported in the proposed method was quite low (15.96 mg/g) [54]. A similar result (adsorption capacity of 13.59 mg/g of Reactive Red 196) was reported when concentrated HCl was used for sawdust treatment [13]. Slightly higher adsorption has also been reported, such as 40.98 mg/g of Drimarine Black CL-B removal by HCl-modified peanut husk [55]. The only exception (a higher removal efficiency) was the treatment of fermentation wastes with nitric acid, where the raw biomass structure was reported to be protonated, replacing the naturally available ionic species, and thereby resulting in a 185.2 mg/g adsorption of Reactive Black 5 [56]. However, there was no following study on the nitric acid treatment.

A combination of amine-based chemicals and acid treatment, such as cationization by dichloroethane and methyl amine, followed by protonation using acetic acid, was also reported in one study to modify the biomass surface [16]. The resultant orange-peel adsorbent showed a maximum adsorption capacity of 163 mg/g of Congo Red. Furthermore, the silylation of biomass was also found to be effective for anionic dye adsorption, where a maximum adsorption of 208.33 mg/g was reported [57]. Moreover, Lin et al. proposed an amphoteric-modification method of delignified wheat straw by a monochloroacetic acid treatment, and then grafting with 2-dimethylamino ethyl methacrylate. The resultant adsorbent could be used to adsorb both anionic and cationic dyes by switching between acidic or alkaline conditions ranging from pH 2 to 10 [58].

Aside from the four major kinds of treatments, some other methods, such as modifications of biomass using oxides and metal salts, have also been reported. For example, the modification of wood biowaste using Al₂O₃ by the solvo-reaction method showed a high adsorption capacity of Reactive Blue 19 (441.9 mg/g) [59]. Furthermore, the modification of sawdust using FeCl₃ (maximum 212.97 mg/g Acid Red G removal) [45], the use
of ZnCl\textsubscript{2} on pulp waste (maximum 285.7 mg/g Methyl Orange removal) [60], hazelnut bagasse (maximum 450 mg/g Acid Blue 350 removal) [61], and pine cone (maximum 118.06 mg/g Alizarin Red S removal) [62], and the use of CaCl\textsubscript{2} with peanut husk (maximum 40.98 mg/g Drimarine Black CL-B removal) [55], have also been reported, showing considerable efficiency.

Overall, the trend in Table 3 shows that effective dye removal by chemically modified adsorbents is more related to the modification methods, rather than to the type of dye. For example, the acidic modification of lignocellulose often produced a lower efficiency either for acid or reactive dyes, although the adsorption capacity was reported to be higher for both when amine-based chemicals were used. When the same adsorbent was used to adsorb acid and reactive dyes, mostly the acid dyes showed a higher removal efficiency [12,51,52], although an exception was also seen [48]. Modification with different amine-based chemicals was found to be more effective for anionic dye adsorption, which was probably related to the abundance of cationic amine groups in these compounds.

### Table 2. Maximum adsorption capacities (q\textsubscript{max}) of anionic dye adsorbents derived from chemically modified agricultural wastes.

| Resources        | Chemical Modification                                           | Modification Type       | Dye                  | q\textsubscript{max} (mg/g) | Reference |
|------------------|------------------------------------------------------------------|-------------------------|----------------------|-----------------------------|-----------|
| Wheat straw      | Grafting with 2-dimethylamino ethyl methacrylate monomer         | Amine-based             | Orange II            | 506                         | [58]      |
| Wheat straw      | Treatment with hexadecylpyridinium bromide                       | Cationic surfactant     | Light Green          | 70.01 ± 3.39                | [47]      |
| Peanut husk      | Modified by hexadecylpyridinium bromide                          | Cationic surfactant     | Light Green          | 60.5                        | [46]      |
| Wheat straw      | Treatment with epichlorohydrin, N,N-dimethylformamide, ethylenediamine, and trimethylamine | Amine-based             | Acid Red 73          | 714.3                       | [12]      |
| Wheat straw      | Treatment with epichlorohydrin, N,N-dimethylformamide, ethylenediamine, and trimethylamine | Amine-based             | Reactive Red 24      | 285.7                       | [12]      |
| Barley straw     | Treatment with hexadecylpyridinium chloride monohydrate          | Cationic surfactant     | Acid Blue 40         | 51.95                       | [49]      |
| Barley straw     | Treatment with hexadecylpyridinium chloride monohydrate          | Cationic surfactant     | Reactive Blue 4      | 31.5                        | [49]      |
| Corn stalks      | Treatment by cetylpyridinium bromide                             | Cationic surfactant     | Acid Red             | 30.77                       | [15]      |
| Corn stalks      | Treatment by cetylpyridinium bromide                             | Cationic surfactant     | Acid Orange          | 31.06                       | [15]      |
| Banana peel      | Reinforcement with nanoparticles and chitosan                    | Amine-based             | Reactive Orange 5    | 125                         | [14]      |
| Sawdust          | Coating with polyaniline                                         | Amine-based             | Acid Red G           | 212.97                      | [45]      |
| Sawdust          | Treatment with cetyltrimethylammonium bromide                    | Cationic surfactant     | Congo Red            | 9.1                         | [50]      |
| Sawdust          | Treatment with concentrate HCl                                   | Acid treatment          | Reactive Red 196     | 13.39                       | [13]      |
| Rice husk        | Treatment with hydroxypropylotadecyldimethylammonium             | Quaternary ammonium compounds | Diamine Green B    | 207.15                      | [52]      |
| Rice husk        | Treatment with hydroxypropylotadecyldimethylammonium             | Quaternary ammonium compounds | Acid Black 24       | 268.88                      | [52]      |
| Rice husk        | Treatment with hydroxypropylotadecyldimethylammonium             | Quaternary ammonium compounds | Congo Red            | 580.09                      | [52]      |
| Peanut husk      | Treatment with alginate and CaCl\textsubscript{2}               | Metal salt              | Drimarine Black CL-B | 40.98                       | [55]      |
| Peanut husk      | Treatment by hexadecylpyridinium bromide in batch mode           | Cationic surfactant     | Light Green          | 146.2 ± 2.4                 | [63]      |
### Table 3. Maximum adsorption capacities ($q_{\text{max}}$) of anionic dye adsorbents derived from chemically modified agricultural wastes.

| Resources                     | Chemical Modification                                      | Modification Type       | Dye                 | $q_{\text{max}}$ (mg/g) | Reference |
|-------------------------------|------------------------------------------------------------|-------------------------|---------------------|--------------------------|-----------|
| Peanut husk                   | Hydrochloric acid treatment                                | Acid treatment          | Drimarine Black CL-B| 51.02                    | [55]      |
| Oil palm empty fruit bunches  | Silylation                                                  | Amine-based             | Procion Red         | 208.33                   | [57]      |
| Orange peel                   | Treatment with dichloroethane, methyl amine, and acetic acid| Amine-based             | Congo Red           | 163                      | [16]      |
| Cotton gin trash              | Cationized by chitosan                                     | Amine-based             | Acid Blue 25        | 151.52                   | [7]       |
| Aquatic plant                 | Phosphoric acid treatment and low-temperature activation   | Acid treatment          | Direct Red 89       | 15.96                    | [54]      |
| Coffee waste                  | Treatment with polyethylenimine                            | Amine-based             | Reactive Black 5    | 77.52                    | [18]      |
| Coffee waste                  | Treatment with polyethylenimine                            | Amine-based             | Congo Red           | 34.36                    | [18]      |
| Hardwood kraft pulp           | Grafting cellulose nanocrystals with ethylenediamine       | Amine-based             | Acid Red GR         | 555.6                    | [44]      |
| Palm kernel shell             | Quaternized by N-(3-chloro-2-hydroxypropyl)trimethylammonium chloride | Quaternary ammonium compounds | Reactive Black 5    | 207.5                    | [53]      |
| Fermentation waste            | Protonated by nitric acid                                  | Acid treatment          | Reactive Black 5    | 185.2                    | [56]      |
| Waste coir pith               | Treatment with hexadecyltrimethylammonium solution         | Cationic surfactant     | Acid Brilliant Blue | 159                      | [51]      |
| Waste coir pith               | Treatment with hexadecyltrimethylammonium solution         | Cationic surfactant     | Procion Orange      | 89                       | [51]      |
| Wood residue                  | Aluminum oxide modification                                | Metal oxide             | Reactive Blue 19    | 29.83                    | [64]      |
| Wood biowaste                 | Aluminum oxide modification                                | Metal oxide             | Reactive Blue 19    | 441.9                    | [59]      |

#### 4.3. Thermal Modifications

The thermal modification of plant-derived wastes is mainly performed to prepare activated carbon (AC). AC is an advanced form of charcoal that is basically a porous carbonaceous structure with an extended surface area [65]. It has been accepted as an effective adsorbent and has been applied widely in water and wastewater treatment, air purification, and solvent recovery, as well as in the pharmaceutical and medical industries and industrial processes. According to a market research report, the market demand for AC was estimated to be USD 5.7 billion worldwide in 2021, and it is predicted to reach USD 8.9 billion by 2026 [66]. A variety of plant-derived wastes have been used as raw materials for the preparation of AC for anionic dye adsorption, as these resources are rich in carbon content, cost effective, renewable, and abundant [67].

Carbonization and activation are basically the two steps that are involved in preparing AC [68]. Activation can be performed by different methods, such as mechanical or thermal, chemical, or a combination of both (i.e., physiochemical) [67], and it can also be biological [69]. These include several methods and their combinations, such as chemical treatment, air oxidation, electrochemical oxidation, and plasma, microwave, and ozone treatment for enhancing the adsorption performance of AC [70–74]. However, for AC prepared for anionic dye adsorption, the chemical-activation technique (using activating agents, such as zinc chloride or phosphoric acid) [75] is mostly preferred (Figure 6) because of its faster activation time, higher carbon yield, simplicity, lower operating temperature, and well-developed pore structure. The proper selection of materials can enhance the
adsorption potentiality of AC through the development of its pore structure (total pore volume, pore size distribution) and surface functionalities [76].

Figure 6. Schematic of thermal-modification steps for plant-derived agricultural waste towards the preparation of activated carbon for anionic dye removal.

The main functional groups on the surface of AC that are responsible for removing dyes are carboxyl, carbonyl, phenols, lactones, and quinones. A positive surface charge on AC can be attained by applying an alkaline treatment, which can accelerate the adsorption of anionic dyes. The porous carbon of alkali-treated AC can enhance the reaction with acid-dye molecules by dipole–dipole, H-bonding, and covalent bonding [69]. As listed in Table 4, ACs prepared from many agricultural byproducts, such as peanut hull, coir pith, rice husk, coffee husk, and water hyacinth, have successfully been used for eliminating anionic dyes from wastewater.

Table 4. Maximum anionic dye adsorptions ($q_{\text{max}}$) reported in different studies onto activated carbon prepared from agricultural waste.

| Resources               | Surface Area (m$^2$/g) | Anionic Dye               | $q_{\text{max}}$ (mg/g) | Reference |
|-------------------------|------------------------|---------------------------|--------------------------|-----------|
| Java citronella         | Not reported           | Congo Red                 | 4.29                     | [77]      |
| Palm tree waste         | 648.90                 | Congo Red                 | 10.4                     | [78]      |
| Water hyacinth          | Not reported           | Congo Red                 | 14.367                   | [79]      |
| Wastewater sludge       | 98.8                   | Amaranth                  | 19.6                     | [80]      |
| Coffee husk             | 613 ± 14               | Indigo Carmine            | 36.63                    | [81]      |
| Carob waste             | 921.07                 | Reactive Black 5          | 36.90                    | [82]      |
| Rick husk               | 272                    | Acid Yellow 36            | 86.9                     | [83]      |
| Pinecone                | 878.07                 | Alizarin Red S            | 118.06                   | [62]      |
| Vegetable waste         | Not reported           | Eriochrome Black T        | 120.50                   | [28]      |
| Date palm fronds        | 431.82                 | Methyl Orange             | 163.132                  | [84]      |
| Sawdust                 | 516.3                  | Acid Yellow 36            | 183.8                    | [85]      |
| Hazelnut bagasse        | 1489                   | Acid Blue 350             | 450                      | [61]      |
| Psyllium stalks          | Not reported           | Coomassie Brilliant Blue  | 237.2                    | [83,85]   |
| Waste potato peels      | Not reported           | Cibacon Blue              | 270.3                    | [83,86]   |
| Pulp waste              | 1022.46                | Methyl Orange             | 285.71                   | [60,85]   |
| Date palm fronds        | 431.82                 | Eriochrome Black T        | 309.59                   | [84]      |
| Grape waste             | 1455                   | Acid yellow 36            | 386                      | [84,87]   |
| Pink shower             | 283.4                  | Congo Red                 | 970                      | [75]      |

The dye-adsorption capacity of different ACs is substantially controlled by the pH of the dye solution, possibly because the electrostatic interaction between ionized dye molecules and carbon surface functionalities that change the solution pH and rate of adsorption also varies. In the case of anionic dye, high dye uptake is favored at a lower pH or acidic medium, as the complete protonation of the carbon surface functionalities enhances the electrostatic attraction with anionic dyes, thereby increasing the dye uptake. From
previous studies, it was observed that the OH group in the solution increased with an increasing pH, producing electrostatic repulsion with anionic dye, and thus decreasing the dye uptake. Therefore, the maximum adsorption of anionic dyes was observed in a pH range of 2–6 [79,84]. Although the surface area of the AC is known as a key factor for dye adsorption because it provides more spaces for the dye molecules to be attached, it can be perceived from Table 4 that this was not always true for anionic dye adsorption due to ionic interactions, which could have a positive or negative impact, depending on the specific adsorption system. For example, the maximum anionic dye absorption (960 mg/g) was found in AC obtained from pink shower seed pods, although it contained a moderate surface area (283.4 m²/g) [75], where the strong electrostatic attraction between the functional groups of the AC surface and anionic dye was facilitated with π–π interactions between the free electrons of the aromatic rings of the Congo Red structure, and the delocalized π-electrons on the basal planes of carbon.

4.4. The Effect of Process Conditions

Other than the modification performed on the biomass, if the amount of adsorbent is kept constant, then different process parameters, which include the pH, temperature, dye concentration, and chemical composition of the biomass, can impact the overall adsorption. The pH of the solution plays a vital role during the adsorption. In numerous studies, for anionic dye adsorption, the favorable pH was reported as 2 [27,30,39,43], and in some cases, even 1 [31,35]. This is directly related to the change in the surface charge in lignocellulose that is altered at a lower pH. A lower pH reduces the electronegativity of the surface, and can even alter it to a positive surface charge [37], thus possibly attracting anionic dyes more conveniently. This was found to be true in cases of different kinds of anionic dyes, such as acid dyes [30,43], reactive dyes [27], and direct dyes [39]. Although this was seen as a common trend, some exceptions were also reported in which the pH showed a minor impact [38], or in which a moderate pH (7.5) was found to be more effective for better adsorption [88].

The bath temperature is also important because a higher temperature can often improve the mobility of dye molecules, and thus, the hindering force from the electronegative adsorbent surface diminishes [89]. As a result, a greater amount of dye can be transported into the adsorbent surface. Added to that, swelling can result in the adsorbent, which can promote intraparticle diffusion inside the structure [89,90], allowing more dyes be adsorbed onto the surface. However, the opposite phenomenon was also frequently reported (exothermic adsorption) [17,37,41], where a higher temperature was unfavorable for dye uptake. This was explained as a possible weakening of the related forces of attraction by a higher temperature [17,40].

The concentration of dye present in a solution largely affects the adsorption rate, and particularly at the initial stage. If the dye concentration is high, then the rate of adsorption will be higher, and vice versa. The content of cellulose in the biomass is also reported as an influencing factor in the adsorption. In a study, three different biomasses (i.e., coconut shells, cauliflower cores, and broccoli stalks) were used for the adsorption of the same anionic dyes, although the chemical compositions of the biomasses were different. The total cellulose, hemicellulose, starch, and pectinic sugar in the cauliflower cores were the highest among the three and resulted in a higher uptake of reactive and acid dyes [89]. Furthermore, the adsorption capacity was particularly significantly affected by the impact of cellulose as the external layer, rather than hemicellulose and lignin [89]. The chemical groups in lignocellulosic biomass (such as –OH, C=O, and C–O) are also good candidates to form hydrogen bonding with anionic dyes [30,43].

5. Adsorption Isotherms

Adsorption isotherms provide dye equilibrium relations that are widely used to assess the appropriateness of an adsorption mechanism. The most commonly used isotherms are
the Langmuir and Freundlich models for any dye adsorption, which have also frequently been used to evaluate anionic dye attachment with plant-derived agricultural wastes.

The Langmuir isotherm model can be linearized as:

\[
\frac{C_e}{q_e} = \frac{C_e}{q_{\text{max}}} + \frac{1}{k_L q_{\text{max}}} (1)
\]

where \(q_e\) is the amount of anionic dye absorbed by the adsorbent at equilibrium; \(C_e\) is the amount of dye left in the solution (mg/L) at the same point; \(q_{\text{max}}\) is the expression of the maximum dye-adsorption capacity (mg/g) by the adsorbent; \(k_L\) is the binding affinity (L/mg), which is also known as the Langmuir constant. The Langmuir constant (\(k_L\)) can be used to derive the suitability of the adsorption system. For example, the equilibrium parameter (\(R_L\)) can be calculated using the value of the \(k_L\) by the following equation [91]:

\[
R_L = \frac{1}{1 + k_L C_0} (2)
\]

where \(C_0\) is the initial dye concentration (mg/L) in the solution before the adsorption begins. The calculated \(R_L\) indicates whether the adsorption system was favorable or not. For instance, if \(0 < R_L < 1\), then the adsorption is favorable, if \(R_L > 1\), then the adsorption is unfavorable, if \(R_L = 1\), then the adsorption is linear, and if \(R_L = 0\), then the adsorption is irreversible.

The other frequently used isotherm is the Freundlich model, which can be linearized as follows [92]:

\[
\ln q_e = \ln k_F - \frac{1}{n} \ln C_e (3)
\]

where \(k_F\) is the adsorption capacity, and \(n\) is the adsorption intensity. The \(n\) value is also used to measure the deviation from the linearity (or heterogeneity). If \(1/n < 1\) (\(n\) ranges from 1 to 10), then the adsorption is counted as favorable, and if \(1/n > 1\), then the adsorption is considered unfavorable. If \(1/n\) is close to zero, then the adsorbent is more heterogeneous, and vice versa [92]. Further indications were also noted from the value of the \(n\), such as \(n = 1\) indicates the linear nature of the adsorption, \(n < 1\) indicates chemical adsorption, and \(n > 1\) indicates physical adsorption [93].

While the Langmuir isotherm is considered more related to monolayer adsorption, the Freundlich isotherm is considered for multilayer adsorption. The coefficient-of-determination (\(R^2\)) values of the Langmuir and Freundlich models listed in Table 5 across different kinds of dyes (acid, reactive, and direct), and after different sorts of modifications (mechanical, chemical, and thermal), show a sporadic result, and often closer values of the \(R^2\) between the Langmuir and Freundlich models. However, as a traditional pattern, often either chemisorption [38,88] or physisorption [7,31] has been claimed as the mechanism of interaction during the adsorption. A combination of multiple mechanisms has also been reported on many occasions. These include different combinations of physical and chemical adsorption [39–41,57], hydrogen bonding [89], ion exchange [34,94], valence forces [58], electrostatic and \(\pi–\pi\) interactions [75], ion exchange and chemical reaction [84], and so on. These interactions were only predicted and were not always confirmed through chemical analysis. Nevertheless, there are great possibilities for many of these interactions during the adsorption. For instance, the zeta potential (\(\zeta\)) of chitosan-modified lignocellulose biomass transformed the \(\zeta\) value from \(-10.8\) mV to +5.1 mV, making it more appropriate for an electrostatic attraction towards anionic dye [7]. Furthermore, because lignocellulose is rich in phenolic groups from lignin, there are chances for \(\pi–\pi\) interactions between the rings present in the anionic dye structure. A schematic representation of different possible dye–adsorbent interactions during anionic dye separation is shown in Figure 7a. The mechanism of adsorption can also differ based on the concentration of dyes. For example, with lower and higher concentrations of dyes, monolayer and multilayer adsorption were observed, respectively [53], while simultaneous monolayer and multilayer adsorption was also reported [84]. Therefore, often the physical interaction between the dye and adsorbent is likely to be combined with chemical interactions, depending on whether there are enough chemical sites present for the reactions and favorable conditions.
Table 5. Reported $R^2$ values of Langmuir and Freundlich isotherm models for anionic dye adsorption.

| Modification Technique | Dye | Adsorbent | R² | Reference |
|------------------------|-----|-----------|----|-----------|
| Mechanical             | Congo Red | Jujuba seeds | 0.999 | 0.987–0.989 | [34] |
| Mechanical             | Reactive Black 5 | Spent mushroom waste | 0.997 | 0.907 | [39] |
| Mechanical             | Cibacron Blue | Ash seed | 0.9357 | 0.98 | [40] |
| Mechanical             | Cibacron Blue | Bean peel | 0.9822 | 0.9414 | [41] |
| Mechanical             | Direct Red 5B | Spent mushroom waste | 0.998 | 0.918 | [39] |
| Mechanical             | Direct Black 22 | Spent mushroom waste | 0.996 | 0.905 | [39] |
| Mechanical             | Acid Blue 25 | Waste tea residue | 0.9197–0.9309 | Not reported | [31] |
| Mechanical             | Congo Red | Bottom ash and deoiled soya | 0.79–0.99 | 0.85–0.97 | [88] |
| Mechanical             | Congo Red | Jute processing Waste | 0.9916 | 0.9912 | [42] |
| Chemical               | Congo Red | Sawdust | 0.9418–0.9867 | 0.9040–0.9876 | [50] |
| Chemical               | Congo Red | Rice husk | 0.9939–0.9988 | 0.9672–0.9861 | [52] |
| Chemical               | Congo Red | Palm tree fiber waste | 0.996 | 0.857 | [78] |
| Chemical               | Congo Red | Coffee Waste | 0.99 | 0.67 | [18] |
| Chemical               | Diamine Green B | Rice husk | 0.9209–0.9731 | 0.8085–0.8988 | [52] |
| Chemical               | Reactive Black 5 | Palm kernel Shell | 0.901 | 0.854 | [53] |
| Chemical               | Reactive Black 5 | Coffee Waste | 0.96 | 0.93 | [18] |
| Chemical               | Reactive Black 5 | Fermentation Wastes | 0.994–0.999 | Not reported | [56] |
| Chemical               | Acid Blue 25 | Cotton gin trash | 0.967–0.996 | 0.875–0.947 | [7] |
| Chemical               | Direct Red 89 | Aquatic Plant | 0.995 | 0.999 | [54] |
| Chemical               | Acid Black 24 | Rice husk | 0.9887–0.9975 | 0.9715–0.9823 | [52] |
| Thermal               | Eriochrome Black T | Date palm Fronds | 0.694–0.953 | 0.711–0.975 | [84] |
| Thermal               | Congo Red | Java Citronella | 0.904–0.957 | 0.994–0.999 | [77] |
| Thermal               | Eriochrome Black T | Vegetable Waste | 0.853–0.978 | 0.965–0.996 | [28] |
Some other less commonly used isotherms for anionic dyes include the Redlich–Peterson model [84], Dubinin–Radushkevich model, Temkin model, and Flory–Huggins model [7].

The Redlich–Peterson model is a three-parameter model, and it is known as a combined form of the Langmuir and Freundlich models. The linear form can be expressed as [84]:

$$\frac{C_e}{q_e} = \frac{1}{K_{RP}} + \frac{a_{RP}}{K_{RP}} C_e^{b_{RP}}$$

where $K_{RP}$ and $a_{RP}$ are the Redlich–Peterson constants, and $b_{RP}$ is an exponent from 0 and 1. The fitting results in a Redlich–Peterson model have occasionally been used for anionic dye adsorption to confirm and represent the adsorption mechanism as a combination of both the Langmuir and Freundlich models [31] (for instance, the simultaneous involvement of monolayer and multilayer adsorption [84]).

The linear form of the Dubinin–Radushkevich isotherm can be expressed as [95]:

$$\ln q_e = \ln q_m - k_{DR} \varepsilon^2$$
where $q_m$ represents the maximum adsorption capacity, $k_{DR}$ is the isotherm constant, and $\varepsilon$ represents the Polanyi potential and is calculated by the following equation:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right)$$  \hspace{1cm} (6)

where $T$ is the equilibrium temperature, and $R$ represents the ideal gas constant $(8.314 \text{ J mol}^{-1} \text{K}^{-1})$ [39]. The isotherm constant ($k_{DR}$) is used to measure the free energy ($E$) of adsorption:

$$E = \frac{1}{\sqrt{2k_{DR}}}$$  \hspace{1cm} (7)

If the $E$ is found to be $< 8 \text{ kJ/mol}$, then this indicates physisorption, and when the $E$ ranges $8–16 \text{ kJ/mol}$, then a chemisorption process is assumed [95]. This isotherm model has sometimes been used to determine between physisorption and chemisorption [39], and to justify the findings from other models [7].

The linear form of the Temkin model can be shown as:

$$q_e = B_1 \ln(k_T C_e)$$  \hspace{1cm} (8)

where $k_T$ is the Temkin constant, and $B_1$ is derived from the below equation:

$$B_1 = \frac{RT}{b_T}$$  \hspace{1cm} (9)

where $b_T$ is another Temkin constant related to the heat of adsorption [45]. From a good fitting with the Temkin model for anionic dye adsorption, the adsorption potential is predicted. The value of the Temkin constants can be used to evaluate the decrease and increase in the binding energy at different adsorption temperatures [45].

The linear equation of the Flory–Huggins model can be expressed as [96]:

$$\ln \left(\frac{\theta}{C_0}\right) = \ln k_{FH} + x \ln(1 - \theta)$$  \hspace{1cm} (10)

where $k_{FH}$ is the Flory–Huggins constant, $x$ represents the remaining dye particles in the adsorption sites, and $\theta$ represents the degree of the adsorbent surface coverage by the dye particles and is derived from the following equation:

$$\theta = 1 - \frac{C_e}{C_0}$$  \hspace{1cm} (11)

When the value of the $k_{FH}$ is positive, a suitable and spontaneous adsorption system is likely [96]. This model can be used to determine the surface coverage of the dye particles onto the adsorbents, although it is used infrequently for anionic dye adsorption [7].

However, as mentioned above, the use of these models was less frequent for anionic dye adsorption compared with the Langmuir and Freundlich isotherms, and they often showed an inferior fitting.

6. Kinetics and Diffusion

The kinetics of anionic dye adsorption on biomass-derived adsorbents has mainly been investigated by pseudo-first-order and pseudo-second-order kinetic models, and often linear equations have been used to draw the plots and find the fitting of the data [18,40,54,57,75]. The first-order model is also known as the Lagergren equation, which relates to the adsorption rate associated with the number of unoccupied areas of the dye [97]. The linear equation of the pseudo-first-order model is represented as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$  \hspace{1cm} (12)
where $k_1$ is the first-order adsorption-rate constant, and $q_t$ is the weight of the dye adsorbed (mg/g) at time ($t$) [98,99]. When the data better fit with the first-order equation, the adsorption is more likely to be a physisorption process.

The pseudo-second-order model is also parallely used with the first-order kinetic model to check the adsorption feasibility. There are four linear equations of this model, which can be derived from each other [92,100]:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e} \quad (13)$$

$$\frac{1}{q_t} = \frac{1}{q_e} + \frac{1}{k_2q_e^2} \left( \frac{1}{t} \right) \quad (14)$$

$$q_t = q_e - \frac{1}{k_2q_e} \left( \frac{q_t}{t} \right) \quad (15)$$

$$\frac{q_t}{t} = k_2q_e^2 - k_2(q_e)q_t \quad (16)$$

where $k_2$ is the second-order adsorption-rate constant. In practice, Equation (13) is comprehensively used. However, after plotting the data, this equation often shows a very good fit (e.g., $R^2 > 0.99$), which is related to the presence of the $t$ value in both the x-axis and y-axis [101]. This can be justified by fitting the same data with another linear equation in which $t$ is not present on both sides and can result in a poor fit (Figure 8). When the data better fit with the second-order equation, the adsorption is more related to a chemisorption process. However, fitting with second-order models for anionic dye adsorbents was often not justified in the literature by plotting with more than one equation when linear models were used. Furthermore, the conversion of the data necessary for the linearization of these kinetic models can also lead to an alteration of the error structure and variation in the weight in data points, and it can also introduce errors into the independent variable [102]. However, using a nonlinear model of second-order kinetics does not alter the kinetic parameters, and thus it is considered to be more accurate and is recommended for estimating the kinetic parameters [103,104].

**Figure 8.** An example of the alteration of the fitting value when graphs were plotted using two different pseudo-second-order equations, showing: (a) good fit, and (b) poor fit from the same data.
The molecular-diffusion mechanism is another key factor in the adsorption rate that cannot be identified by the pseudo models. If the adsorption is a physisorption phenomenon, then there is more possibility that the diffusion is the rate-controlling step [101]. In an adsorbent/dye-solution adsorption process, the transfer of dye particles into the adsorbent can be controlled by one of the three known mechanisms: film diffusion, intraparticle diffusion, or a combination of both [105]. Film diffusion is the transfer of dye particles to the adsorbent surface, and intraparticle diffusion is the diffusion of dye particles into the adsorbent pores (Figure 7b). It was reported that both film diffusion (also known as external mass transfer) and intraparticle diffusion can play a significant role during anionic dye adsorption [35].

The linear form of the intraparticle-diffusion model can be expressed as [92]:

\[ q_t = k_{ID}\cdot t^{1/2} + C \]  

(17)

where \( k_{ID} \) represents the diffusion-rate constant, and \( C \) is the thickness of the boundary layer (Figure 7b). If \( C \) is considerably higher, then a superior influence of the surface adsorption on the adsorption rate is likely [106]. As per this model, if the fitted line goes through the origin (0, 0), then this is a sign of the sole control of intraparticle diffusion [107]. However, in most cases, more than one step of adsorption is observed from the plotting of the intraparticle-diffusion model. These include the initial film diffusion, followed by intraparticle diffusion, and possibly a third and slow adsorbing stage close to an equilibrium.

7. Thermodynamics of Adsorption

Thermodynamic studies of dye adsorption are performed when the adsorption is conducted at different temperatures. From the pseudo-second-order constant (\( k_2 \)), the activation energy (\( E_a \)) of the adsorption process can be determined by the Arrhenius equation:

\[ \ln k_2 = \ln A - \frac{E_a}{RT} \]  

(18)

where \( A \) is the Arrhenius factor, \( E_a \) is the Arrhenius activation energy (kJ/mol), \( T \) represents the absolute temperature (K), and \( R \) represents the gas constant [99].

The entropy (\( \Delta S^\circ \)) and enthalpy (\( \Delta H^\circ \)) are derived using the Eyring formula, which is expressed as:

\[ \ln \left( \frac{k_2}{T} \right) = \ln \left( \frac{K_b}{h} \right) + \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \]  

(19)

where \( K_b \) is the Boltzman constant, and \( h \) is the Planck constant. A positive value of the \( \Delta H^\circ \) indicates an endothermic reaction (adsorption increases with increasing temperature) [39], while a negative value of the \( \Delta H^\circ \) indicates an exothermic process (adsorption decreases with increasing temperature) [100]. A positive value of the \( \Delta S^\circ \) indicates a decrease in the randomness of solid/liquid interfaces, and vice versa [39].

Finally, the Gibbs energy of activation (\( \Delta G^\circ \)) is calculated from the following formula:

\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \]  

(20)

A positive value of the \( \Delta G^\circ \) indicates nonspontaneous reactions, which need an input of energy, while a negative value of the \( \Delta G^\circ \) indicates spontaneous reactions, which can continue without external energy [108].

Thermodynamic studies have been extensively conducted for anionic dye adsorption, and the values of the \( \Delta S^\circ, \Delta H^\circ, \text{ and } \Delta G^\circ \) have been used to determine whether the process is spontaneous/nonspontaneous and exothermic/endothemic, as well as the randomness in the adsorbent/solution interfaces. As shown in Table 6, in most cases, the mechanism was found to be spontaneous (negative \( \Delta G^\circ \)) for either kind of dye or the modification methods. Although the endothermic process (negative \( \Delta H^\circ \)) was more observed, the
exothermic process (positive ΔH°) was also seen. In most cases, positive ΔS° was also seen, which means more uniformity during the anionic dye adsorption.

Table 6. The trends of the enthalpy (ΔH°), Gibbs energy of activation (ΔG°), and entropy (ΔS°) of anionic dye adsorption onto plant-derived agricultural waste.

| Adsorbent                        | Modification Technique | Dye                | ΔH° (kJ/mol) | ΔG° (kJ/mol) | ΔS° (J/mol K) | References |
|----------------------------------|------------------------|--------------------|--------------|--------------|---------------|------------|
| Bean peel                        | Mechanical             | Cibacron Blue      | −32.36       | −3.97 to −4.89 | −92.21        | [41]       |
| Ash seed                         | Mechanical             | Cibacron Blue      | −28.95       | −18.01 to −18.37 | −35.36        | [40]       |
| Spent mushroom waste             | Mechanical             | Direct Red 5B      | 0.99         | −0.79 to −1.83 | 1.63          | [39]       |
| Spent mushroom waste             | Mechanical             | Direct Black 22    | 0.59         | −0.69 to −1.33 | 1.65          | [39]       |
| Spent mushroom waste             | Mechanical             | Direct Black 71    | 3.79         | −3.32 to −7.47 | 7.02          | [39]       |
| Spent mushroom waste             | Mechanical             | Reactive Black 5   | 0.62         | −0.15 to −0.77 | 0.21          | [39]       |
| Vegetable waste                  | Mechanical             | Eriochrome Black T | 44.51        | −2.72 to −5.89 | 158.51        |            |
| Jujuba seeds                     | Mechanical             | Congo Red          | 12.94        | −3.49 to −6.43 | 57.9          | [34]       |
| Sawdust                          | Chemical               | Acid Red G         | 28.7         | −1.07 to −3.14 | 103.4         | [45]       |
| Orange peel                      | Chemical               | Congo Red          | 19           | −1.88 to −3.23 | 70            | [16]       |
| Peanut husk                      | Chemical               | Drimarine Black CL-B | −23.74       | −0.22 to −2.9  | 72            | [55]       |
| Coffee waste                     | Chemical               | Reactive Black 5   | 8.28         | −9.66 to −11.08 | 59.99        | [18]       |
| Coffee waste                     | Chemical               | Congo Red          | 35.05        | −3.76 to −8.17 | 130.59        | [18]       |
| Rice husk                        | Chemical               | Diamine Green B    | 15.06        | −3.46 to −4.39 | 35.11         | [52]       |
| Rice husk                        | Chemical               | Acid Black 24      | 16.32        | −2.65 to −3.10 | 43.52         | [52]       |
| Rice husk                        | Chemical               | Congo Red          | 2.96         | −2.98 to −3.37 | 19.57         | [52]       |
| Wheat straw                      | Chemical               | Reactive Red 24    | 4.53         | −29.05 to −32.93 | 135.1        | [12]       |
| Waste coir pith                  | Chemical               | Procion Orange     | 25.69        | −8.43 to −11.15 | 111.52        | [51]       |
| Waste coir pith                  | Chemical               | Acid Brilliant Blue| 70.09        | −5.65 to −11.37 | 245.64        | [51]       |
| Water hyacinth                   | Thermal                | Congo Red          | −189.01 to −918.94 | −3001.04 to −12,254.1 | 16.39 to 53.97 | [79] |
| Coffee husk                      | Thermal                | Indigo Carmine     | 21.72 to 35.83 | −46.71 to −61.05 | 229.9 to 287.6 | [81] |
| Java citronella                  | Thermal                | Congo Red          | −0.007 to −0.029 | 7.9 to 30.2   | −6 to −92    | [77]       |
| Pinecone                         | Thermal                | Alizarin Red S     | 29.13        | −2.75 to −4.39 | 82            | [62]       |
| Vegetable waste                  | Thermal                | Eriochrome Black T | −10.08       | −2.76 to 3.43 | −22.32        | [28]       |
8. Circularity and Sustainability

To prove the adsorbents as sustainable and economically viable, the circularity of the adsorbents has received significant attention. In this regard, the regeneration ability of the adsorbents is a key criterion. If the adsorbed dyes can be successfully desorbed from the adsorbent, then the reuse of both the adsorbent and dye could be possible, and the process becomes more economically feasible [34]. Regeneration studies have been widely considered for anionic dye adsorbents, and the results are promising. These are often performed by altering the pH of the solution. When anionic dyes are physically bound to the adsorbent, an alteration of the pH, often alkaline [33], could be more useful to transfer them into the solution [7]. For example, a desorption experiment using different components (i.e., water, HCl, acetic acid, NaOH, and ethanol) showed a maximum Methyl Orange desorption of 67.85\% by a NaOH solution, while the second best was 34.5\% by acetic acid [60]. This was also confirmed by different studies in which a 45 min treatment of the adsorbent with 0.1 M NaOH at 20 °C was enough to desorb most of the anionic dyes and reuse the adsorbents [7,109]. In many studies, the regeneration of anionic dyes and the reuse of the adsorbents were proven highly feasible. For example, 45 consecutive cycles from sawdust adsorbent were reported [45], while at least 3 cycles were possible by a cotton-gin-trash bioadsorbent [7] and activated carbon prepared from pine cone [62]. Although high desorption efficiencies, such as 98\% [16] or 83.7–90.3\% dye desorption, have been reported [77], a lower desorption rate, such as 35–43\%, was also reported when the dyes were attached with adsorbent through a chemical reaction (chemisorption) [15]. However, more than half of the studies on anionic dye removal have considered desorption studies to justify the effectiveness of the proposed adsorbents, which shows the requirement for sustainability. From an economic evaluation, it was reported that the cost for the preparation and regeneration of adsorbents of biomass waste (USD 42.43/kg) was significantly lower than commercially available activated carbon (USD 111.37/kg) [60]. From both the economic and environmental points of view, the adsorbents prepared from natural plant-derived agricultural wastes seem to be more sustainable, as, on the one hand, they reduce the process cost, and, on the other hand, they diminish the amount of waste from the environment. The use of these adsorbents in a circular manner by successful regeneration is further beneficial. When the adsorbents reach their end of life, the dyes can be desorbed and, as the adsorbents are biodegradable, they can be discarded into the land without any hazard. Overall, the extent of the dye-desorption studies conducted along with the adsorption of anionic dyes indicates the urgency of making these bioadsorbents more sustainable and efficient, validating their more feasible use in the future.

9. Conclusions and Future Scopes

Anionic dyes are widely used in different applications and are one of the major contaminants in dye wastewater. Over the years, lignocellulosic agricultural wastes have been widely used to remove these dyes from wastewater. Adsorbing anionic dyes by these adsorbents is challenging, as they inherently possess some repulsing effect on anionic dyes due to their electronegative surfaces. Nevertheless, given the low cost and abundance of these natural resources, researchers have frequently made them capable of anionic dye adsorption by mechanical, chemical, and thermal modifications. In cases in which only mechanical modifications are performed, adjusting the bath solution to a lower pH can enhance the dye adsorption. Reducing the particle size and tuning the temperature to a favorable condition can also promote dye adsorption. Although thermal modification, such as transformation into activated carbon, showed an improvement in the adsorption, chemically modifying the surface by inducing new cationic groups was found to be the most effective method of anionic dye removal when using these resources. The chemical modification of these biomasses was most successful when using amine-based and quaternary ammonium compounds. It is worth mentioning that quaternary ammonium compounds often possess environmental hazards, while amine-based compounds can also be hazardous, and thus require careful attention. Even though the use of amine-rich
nonhazardous biopolymers, such as chitosan and its derivatives, have been well explored for the removal of anionic dyes, they are not widely considered for the modifications of lignocellulosic biomass (with a few exceptions), which could be a future research area. Furthermore, when the efficiency of a chemically modified biomass adsorbent was reported, often it was not paralleled compared with the chemically unmodified biomass. Thus, the degree of improvement in the dye adsorption was often not identified. However, the extent of regeneration studies shows the keen attention of researchers to not only just proposing an adsorbent to separate anionic dyes, but also to proving its sustainability in terms of cost reduction and effectiveness. The success trend portrays the promising future of using these abundant wastes as the key resources for the essential separation of anionic dyes.

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