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Review

# 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



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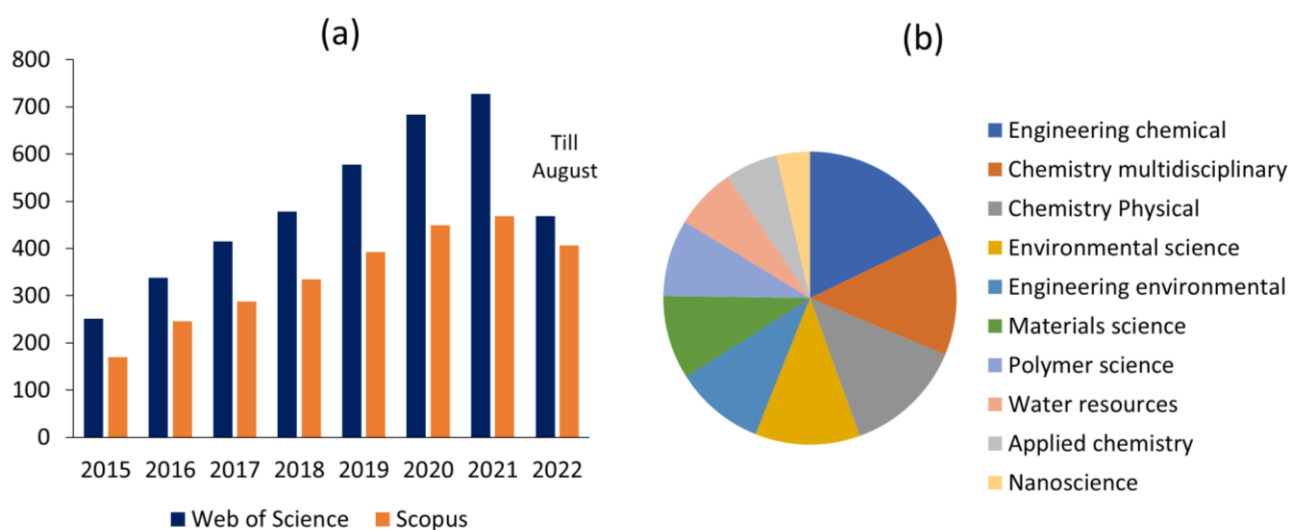


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## 1. Introduction

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

Scopus): 3938 have been published from 2015 to the present (~79%), and 2457 have been published from just 2019 to the present date (~49%). These studies have been performed across varied disciplines, such as from the engineering, environmental, chemistry, and materials perspectives, which shows the urge to solve the problem from multiple sectors (Figure 1).



**Figure 1.** The number of studies retrieved from the Web of Science and Scopus databases: (a) on ‘anionic dye removal’ since 2015, and (b) their distribution across ten key subject categories.

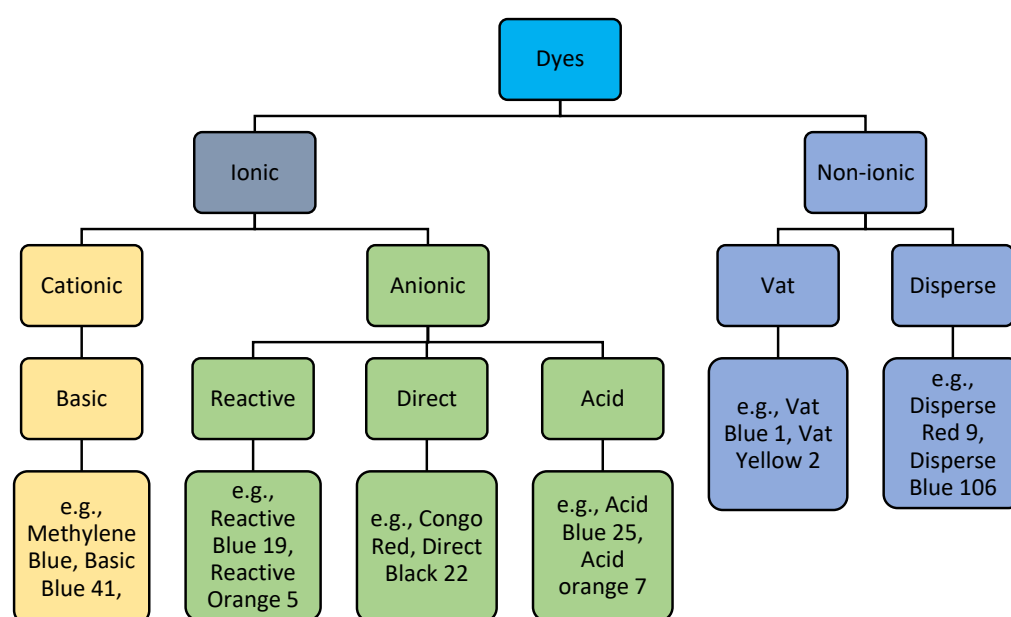
Many techniques are proposed for removing anionic dyes from wastewater, such as physical (membrane filtration, ion exchange, irradiation, coagulation), chemical (oxidation, ozonation, photochemical, electrochemical destruction), and biological (aerobic and anaerobic microbial degradation) treatments [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.



**Figure 2.** Ion-based-dye classification with examples.

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<sub>2</sub>) [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.

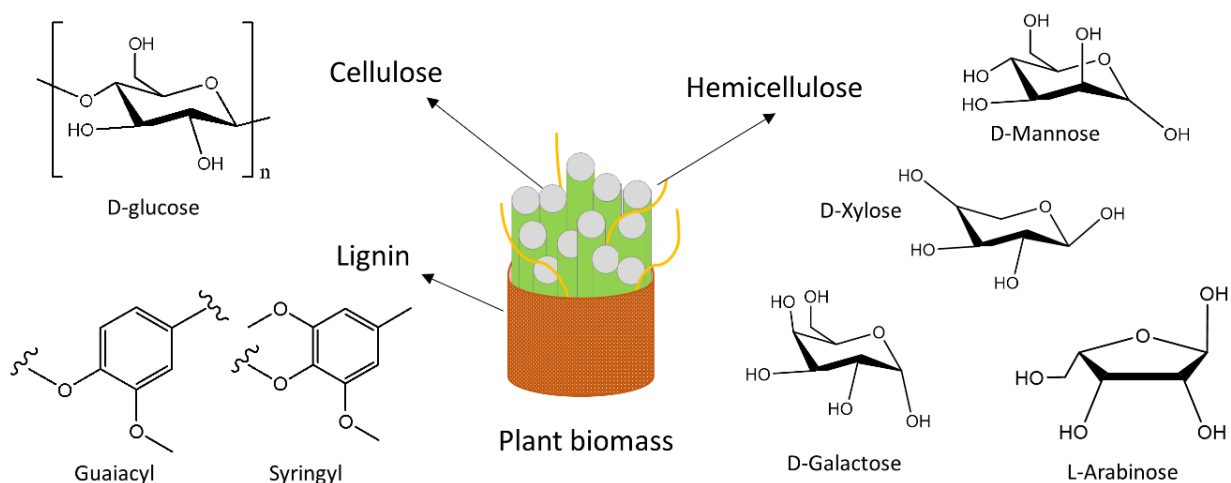


Figure 3. Common chemical groups in plant-derived agricultural waste.

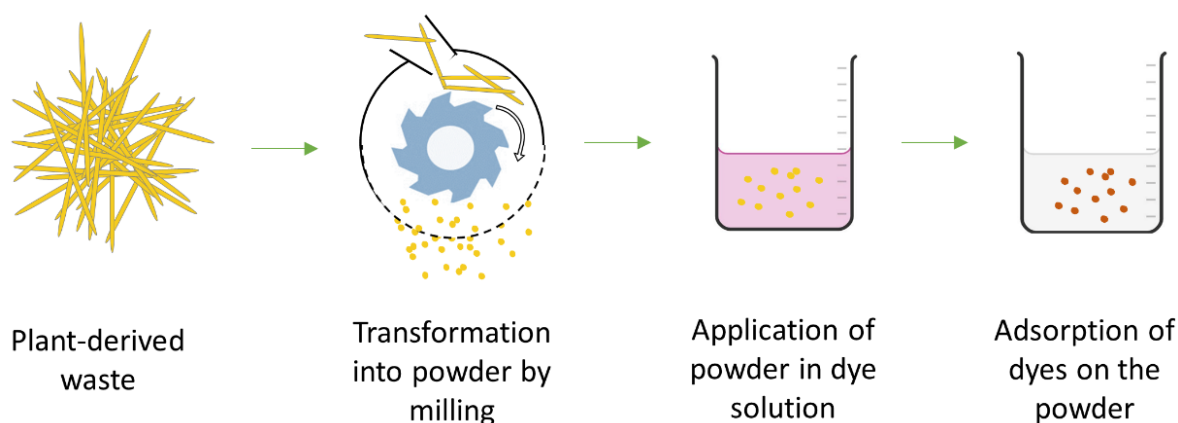
## 4. Adsorbents for Anionic Dyes

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.

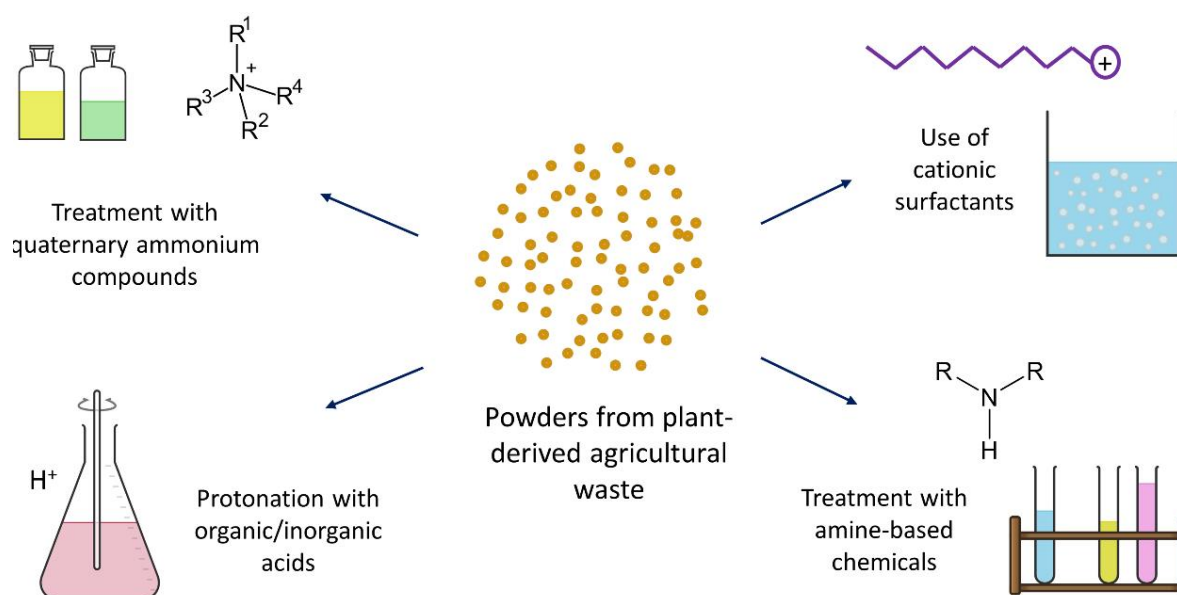
**Table 1.** Maximum adsorption capacities ( $q_{\max}$ ) of anionic dye adsorbents derived from mechanically modified agricultural wastes.

Resources	Particle Size ( $\mu\text{m}$ )	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]
<i>Saccharomyces cerevisiae</i> (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	$\leq 1000$	Cibacron Blue	67.114	[40]
Bean peel	$\leq 1000$	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  $\mu\text{m}$  to <100  $\mu\text{m}$  [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.



**Figure 5.** Different chemical-treatment methods are proposed for modifying plant-derived agricultural waste.

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 NaBH<sub>4</sub> at room temperature for 3 h, which resulted in the 555.6 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 ((FeCl<sub>3</sub>). The inclusion of polyaniline nanofibers enhanced the surface area of the biomass (from 1.22 to 16.26 m<sup>2</sup>/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  $146.2 \pm 2.4$  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 hydroxypropyloctadecyldimethylammonium-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 13.39 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  $\text{Al}_2\text{O}_3$  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  $\text{FeCl}_3$  (maximum 212.97 mg/g Acid Red G removal) [45], the use

of ZnCl<sub>2</sub> 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<sub>2</sub> 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 ( $q_{\max}$ ) of anionic dye adsorbents derived from chemically modified agricultural wastes.

Resources	Chemical Modification	Modification Type	Dye	$q_{\max}$ (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 hydroxypropyloctadecyldimethylammonium	Quaternary ammonium compounds	Diamine Green B	207.15	[52]
Rice husk	Treatment with hydroxypropyloctadecyldimethylammonium	Quaternary ammonium compounds	Acid Black 24	268.88	[52]
Rice husk	Treatment with hydroxypropyloctadecyldimethylammonium	Quaternary ammonium compounds	Congo Red	580.09	[52]
Peanut husk	Treatment with alginate and CaCl <sub>2</sub>	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 ( $q_{\max}$ ) of anionic dye adsorbents derived from chemically modified agricultural wastes.

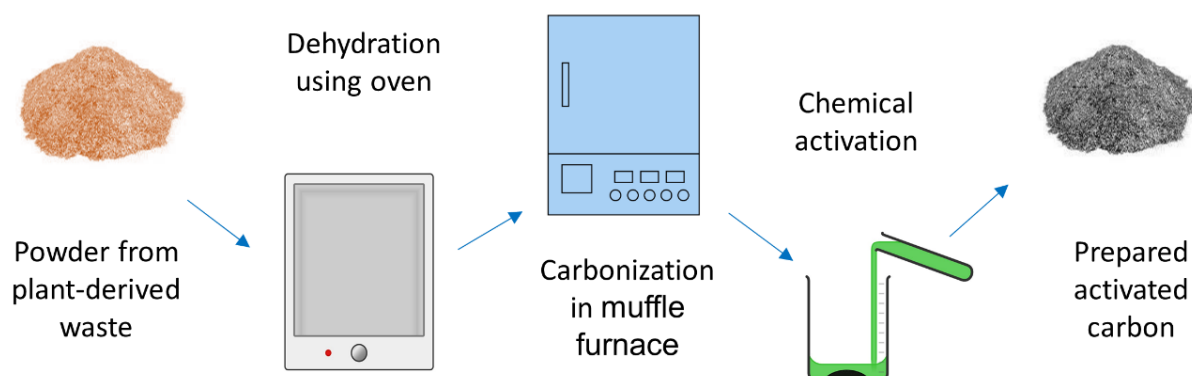
Resources	Chemical Modification	Modification Type	Dye	$q_{\max}$ (mg/g)	Reference
Peanut husk	Hydrochloric acid treatment	Acid treatment	Drimarine Black CL-B	51.02	[55]
Oil palm empty fruit bunches	Silylation	Amine-based	Procion Red	208.33	[57]
Orange peel	Treatment with dichloroethane, methyl amine, 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 ( $q_{\max}$ ) reported in different studies onto activated carbon prepared from agricultural waste.

Resources	Surface Area ( $\text{m}^2/\text{g}$ )	Anionic Dye	$q_{\max}$ (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	$613 \pm 14$	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	[83]
Hazelnut bagasse	1489	Acid Blue 350	450	[61]
Psyllium stalks	Not reported	Coomassie Brilliant Blue	237.2	[83,85]
Waste potato peels	Not reported	Cibacron 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 m<sup>2</sup>/g) [75], where the strong electrostatic attraction between the functional groups of the AC surface and anionic dye was facilitated with  $\pi$ – $\pi$  interactions between the free electrons of the aromatic rings of the Congo Red structure, and the delocalized  $\pi$ -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:

$$C_e/q_e = C_e/q_{\max} + 1/(k_L q_{\max}) \quad (1)$$

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;  $q_{\max}$  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]:

$$R_L = 1/(1 + k_L C_0) \quad (2)$$

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]:

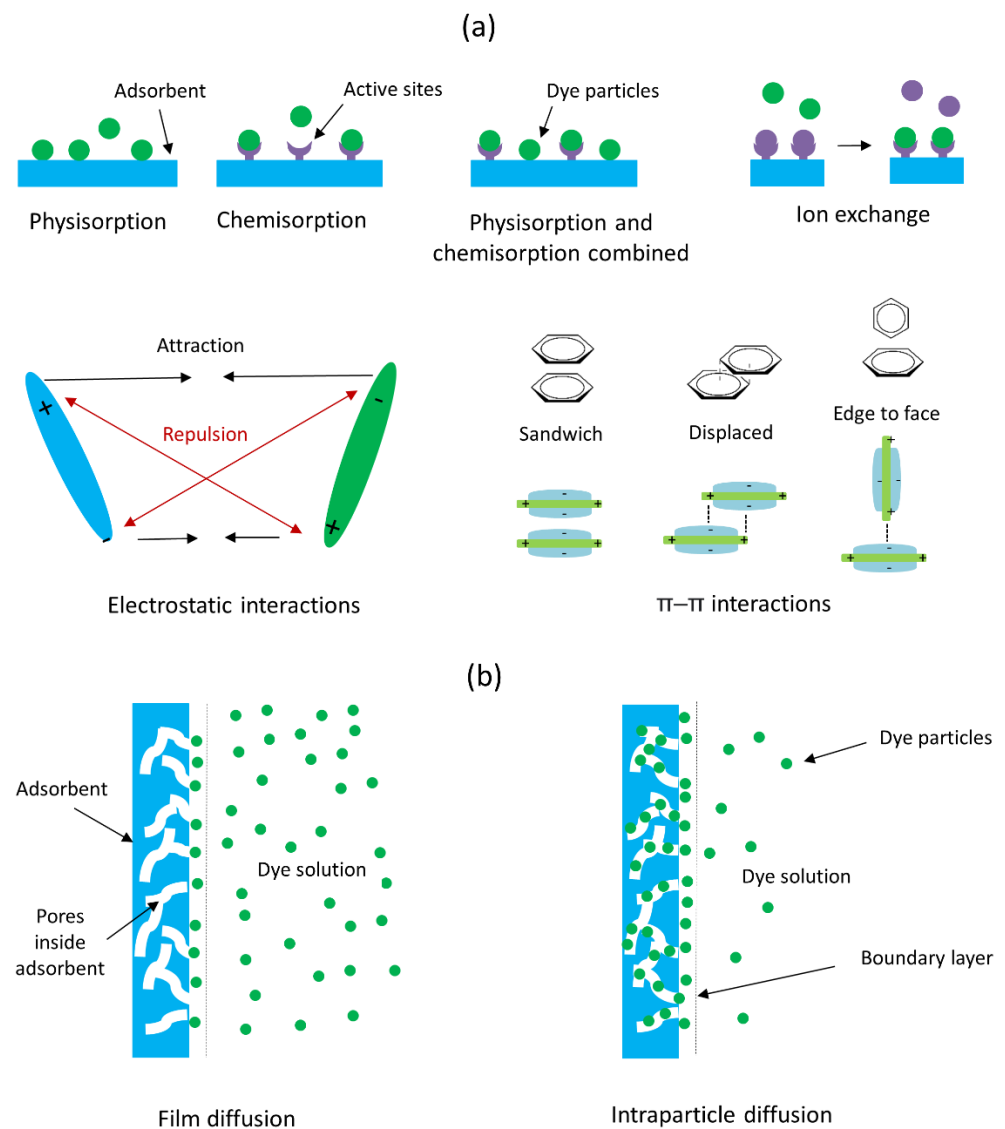
$$\ln q_e = \ln k_F - (1/n) \ln C_e \quad (3)$$

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<sup>2</sup> values of Langmuir and Freundlich isotherm models for anionic dye adsorption.

Modification Technique	Dye	Adsorbent	R <sup>2</sup>		Reference
			Langmuir Model	Freundlich Model	
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]



**Figure 7.** Schematic representations of: (a) different interactions between dye particles and lignocellulosic biomass; (b) diffusion mechanism of dye particles during an adsorption process by a biomass-derived adsorbent.

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]:

$$\frac{C_e}{q_e} = \frac{1}{K_{RP}} + \frac{a_{RP}}{K_{RP}} C_e^{b_{RP}} \quad (4)$$

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]:

$$\ln q_e = \ln q_m - k_{DR} \epsilon^2 \quad (5)$$



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:

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

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

$$E = 1/\sqrt{2k_{DR}} \quad (7)$$

If the  $E$  is found to be  $<8 \text{ kJ/mol}$ , then this indicates physisorption, and when the  $E$  ranges  $8\text{--}16 \text{ kJ/mol}$ , 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:

$$q_e = B_1 \ln(k_T C_e) \quad (8)$$

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

$$B_1 = \frac{RT}{b_T} \quad (9)$$

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]:

$$\ln \frac{\theta}{C_0} = \ln k_{FH} + x \ln(1 - \theta) \quad (10)$$

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:

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

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:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (12)$$

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 parallelly 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]:

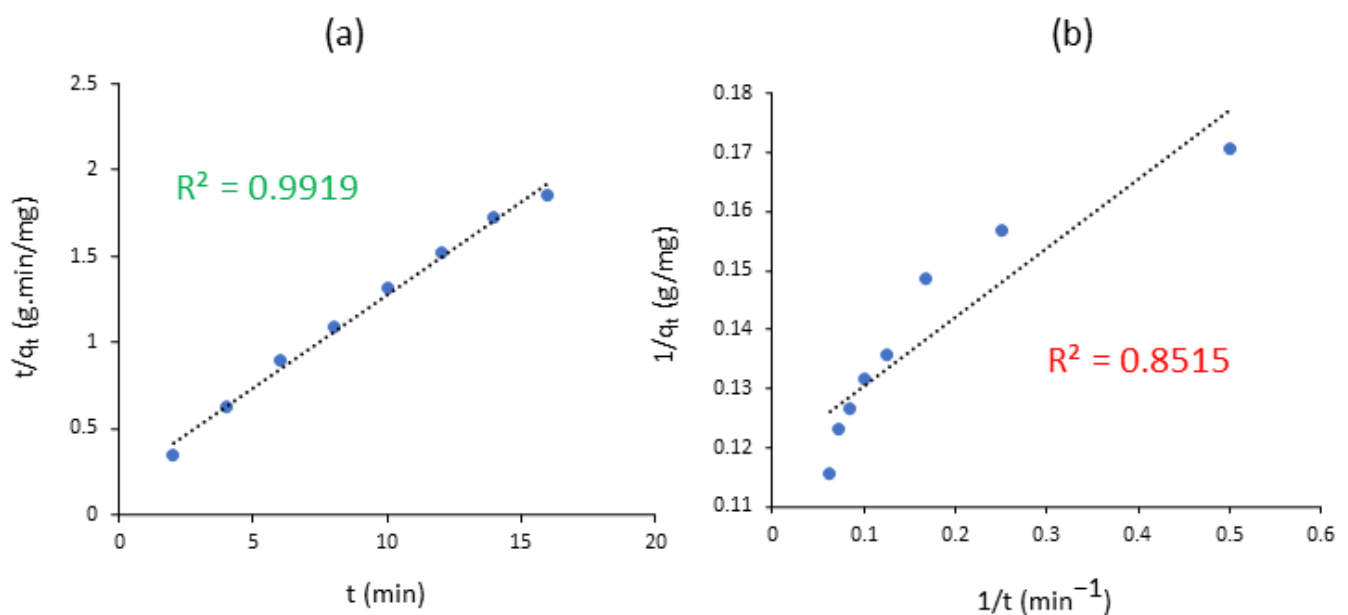
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (13)$$

$$\frac{1}{q_t} = \frac{1}{q_e} + \frac{1}{k_2 q_e^2} \left( \frac{1}{t} \right) \quad (14)$$

$$q_t = q_e - \frac{1}{k_2 q_e} \left( \frac{q_t}{t} \right) \quad (15)$$

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

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]:

$$q_t = k_{ID} \cdot t^{1/2} + C \quad (17)$$

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:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (18)$$

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:

$$\ln \left( \frac{k_2}{T} \right) = \ln \left( \frac{K_b}{h} \right) + \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (19)$$

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:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (20)$$

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  $\Delta S^\circ$ ,  $\Delta H^\circ$ , and  $\Delta G^\circ$  have been used to determine whether the process is spontaneous/nonspontaneous and exothermic/endothermic, 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  $\Delta H^\circ$ ) was also seen. In most cases, positive  $\Delta S^\circ$  was also seen, which means more uniformity during the anionic dye adsorption.

**Table 6.** The trends of the enthalpy ( $\Delta H^\circ$ ), Gibbs energy of activation ( $\Delta G^\circ$ ), and entropy ( $\Delta S^\circ$ ) of anionic dye adsorption onto plant-derived agricultural waste.

Adsorbent	Modification Technique	Dye	$\Delta H^\circ$ (kJ/mol)	$\Delta G^\circ$ (kJ/mol)	$\Delta S^\circ$ (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 parallelly 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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## References

1. Haque, A.N.M.A.; Remadevi, R.; Wang, X.; Naebe, M. Sorption properties of fabricated film from cotton gin trash. *Mater. Today Proc.* **2020**, *31*, S221–S226. [[CrossRef](#)]
2. Hassan, M.M.; Carr, C.M. A critical review on recent advancements of the removal of reactive dyes from dyehouse effluent by ion-exchange adsorbents. *Chemosphere* **2018**, *209*, 201–219. [[CrossRef](#)]
3. Lellis, B.; Fávaro-Polonio, C.Z.; Pamphile, J.A.; Polonio, J.C. Effects of textile dyes on health and the environment and bioremediation potential of living organisms. *Biotechnol. Res. Innov.* **2019**, *3*, 275–290. [[CrossRef](#)]
4. Salleh, M.A.M.; Mahmoud, D.K.; Karim, W.A.W.A.; Idris, A. Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review. *Desalination* **2011**, *280*, 1–13. [[CrossRef](#)]
5. Haque, A.N.M.A.; Remadevi, R.; Rojas, O.J.; Wang, X.; Naebe, M. Kinetics and equilibrium adsorption of methylene blue onto cotton gin trash bioadsorbents. *Cellulose* **2020**, *27*, 6485–6504. [[CrossRef](#)]
6. Ray, R.C.; Behera, S.S. Solid state fermentation for production of microbial cellulases. In *Biotechnology of Microbial Enzymes*; Elsevier: Amsterdam, The Netherlands, 2017; pp. 43–79.
7. Haque, A.N.M.A.; Remadevi, R.; Wang, X.; Naebe, M. Adsorption of anionic Acid Blue 25 on chitosan-modified cotton gin trash film. *Cellulose* **2020**, *27*, 9437–9456. [[CrossRef](#)]
8. Roa, K.; Oyarce, E.; Boulett, A.; ALSamman, M.; Oyarzún, D.; Pizarro, G.D.C.; Sánchez, J. Lignocellulose-based materials and their application in the removal of dyes from water: A review. *Sustain. Mater. Technol.* **2021**, *29*, e00320. [[CrossRef](#)]
9. Mishra, S.; Cheng, L.; Maiti, A. The utilization of agro-biomass/byproducts for effective bio-removal of dyes from dyeing wastewater: A comprehensive review. *J. Environ. Chem. Eng.* **2021**, *9*, 104901. [[CrossRef](#)]
10. Mo, J.; Yang, Q.; Zhang, N.; Zhang, W.; Zheng, Y.; Zhang, Z. A review on agro-industrial waste (AIW) derived adsorbents for water and wastewater treatment. *J. Environ. Manag.* **2018**, *227*, 395–405. [[CrossRef](#)]
11. Rachna, K.; Agarwal, A.; Singh, N. Rice husk and Sodium hydroxide activated Rice husk for removal of Reactive yellow dye from water. *Mater. Today Proc.* **2019**, *12*, 573–580. [[CrossRef](#)]
12. Xu, X.; Gao, B.-Y.; Yue, Q.-Y.; Zhong, Q.-Q. Preparation and utilization of wheat straw bearing amine groups for the sorption of acid and reactive dyes from aqueous solutions. *J. Hazard. Mater.* **2010**, *182*, 1–9. [[CrossRef](#)] [[PubMed](#)]
13. Doltabadi, M.; Alidadi, H.; Davoudi, M. Comparative study of cationic and anionic dye removal from aqueous solutions using sawdust-based adsorbent. *Environ. Prog. Sustain. Energy* **2016**, *35*, 1078–1090. [[CrossRef](#)]
14. Abdelghaffar, F. Biosorption of anionic dye using nanocomposite derived from chitosan and silver Nanoparticles synthesized via cellulosic banana peel bio-waste. *Environ. Technol. Innov.* **2021**, *24*, 101852. [[CrossRef](#)]
15. Soldatkina, L.; Zavrichko, M. Equilibrium, kinetic, and thermodynamic studies of anionic dyes adsorption on corn stalks modified by cetylpyridinium bromide. *Colloids Interfaces* **2018**, *3*, 4. [[CrossRef](#)]
16. Munagapati, V.S.; Kim, D.-S. Adsorption of anionic azo dye Congo Red from aqueous solution by Cationic Modified Orange Peel Powder. *J. Mol. Liq.* **2016**, *220*, 540–548. [[CrossRef](#)]

17. Tahir, M.A.; Bhatti, H.N.; Iqbal, M. Solar Red and Brittle Blue direct dyes adsorption onto Eucalyptus angophoroides bark: Equilibrium, kinetics and thermodynamic studies. *J. Environ. Chem. Eng.* **2016**, *4*, 2431–2439. [[CrossRef](#)]
18. Wong, S.; Ghafar, N.A.; Ngadi, N.; Razmi, F.A.; Inuwa, I.M.; Mat, R.; Amin, N.A.S. Effective removal of anionic textile dyes using adsorbent synthesized from coffee waste. *Sci. Rep.* **2020**, *10*, 2928. [[CrossRef](#)]
19. Broadbent, A.D. *Basic Principles of Textile Coloration*; Society of Dyers and Colorists Bradford: Bradford, UK, 2001; Volume 132.
20. Khatri, A.; Peerzada, M.H.; Mohsin, M.; White, M. A review on developments in dyeing cotton fabrics with reactive dyes for reducing effluent pollution. *J. Clean. Prod.* **2015**, *87*, 50–57. [[CrossRef](#)]
21. Haque, A.N.M.A.; Islam, M.A. The contribution of different vinyl sulphone-reactive dyes to an effluent. *J. Taibah Univ. Sci.* **2015**, *9*, 594–600. [[CrossRef](#)]
22. Sekar, N. Acid dyes. In *Handbook of Textile and Industrial Dyeing: Principles, Processes and Types of Dyes*; Clark, M., Ed.; Woodhead Publishing Limited: Cambridge, UK, 2011; pp. 486–514.
23. Chakraborty, J. *Fundamentals and Practices in Colouration of Textiles*; CRC Press: Boca Raton, FL, USA, 2015.
24. Haque, A.N.M.A.; Zhang, Y.; Naebe, M. A review on lignocellulose/poly (vinyl alcohol) composites: Cleaner approaches for greener materials. *Cellulose* **2021**, *28*, 10741–10764. [[CrossRef](#)]
25. Haque, A.N.M.A.; Remadevi, R.; Naebe, M. Lemongrass (Cymbopogon): A review on its structure, properties, applications and recent developments. *Cellulose* **2018**, *25*, 5455–5477. [[CrossRef](#)]
26. Sanderson, K. Lignocellulose: A chewy problem. *Nature* **2011**, *474*, S12–S14. [[CrossRef](#)] [[PubMed](#)]
27. Değermenci, G.D.; Değermenci, N.; Ayvaoglu, V.; Durmaz, E.; Çakır, D.; Akan, E. Adsorption of reactive dyes on lignocellulosic waste; characterization, equilibrium, kinetic and thermodynamic studies. *J. Clean. Prod.* **2019**, *225*, 1220–1229. [[CrossRef](#)]
28. Aziz, E.K.; Abdelmajid, R.; Rachid, L.M.; Mohammadine, E.H. Adsorptive removal of anionic dye from aqueous solutions using powdered and calcined vegetables wastes as low-cost adsorbent. *Arab. J. Basic Appl. Sci.* **2018**, *25*, 93–102. [[CrossRef](#)]
29. Rodríguez, A.; García, J.; Ovejero, G.; Mestanza, M. Adsorption of anionic and cationic dyes on activated carbon from aqueous solutions: Equilibrium and kinetics. *J. Hazard. Mater.* **2009**, *172*, 1311–1320. [[CrossRef](#)]
30. Stavrinou, A.; Aggelopoulos, C.; Tsakiroglou, C. Exploring the adsorption mechanisms of cationic and anionic dyes onto agricultural waste peels of banana, cucumber and potato: Adsorption kinetics and equilibrium isotherms as a tool. *J. Environ. Chem. Eng.* **2018**, *6*, 6958–6970. [[CrossRef](#)]
31. Jain, S.N.; Tamboli, S.R.; Sutar, D.S.; Jadhav, S.R.; Marathe, J.V.; Shaikh, A.A.; Prajapati, A.A. Batch and continuous studies for adsorption of anionic dye onto waste tea residue: Kinetic, equilibrium, breakthrough and reusability studies. *J. Clean. Prod.* **2020**, *252*, 119778. [[CrossRef](#)]
32. El Messaoudi, N.; Dbik, A.; El Khomri, M.; Sabour, A.; Bentahar, S.; Lacherai, A. Date stones of Phoenix dactylifera and jujube shells of Ziziphus lotus as potential biosorbents for anionic dye removal. *Int. J. Phytoremediat.* **2017**, *19*, 1047–1052. [[CrossRef](#)]
33. Namasivayam, C.; Prabha, D.; Kumutha, M. Removal of direct red and acid brilliant blue by adsorption on to banana pith. *Bioresour. Technol.* **1998**, *64*, 77–79. [[CrossRef](#)]
34. Reddy, M.S.; Sivaramakrishna, L.; Reddy, A.V. The use of an agricultural waste material, Jujuba seeds for the removal of anionic dye (Congo red) from aqueous medium. *J. Hazard. Mater.* **2012**, *203*, 118–127. [[CrossRef](#)]
35. Tunç, Ö.; Tanacı, H.; Aksu, Z. Potential use of cotton plant wastes for the removal of Remazol Black B reactive dye. *J. Hazard. Mater.* **2009**, *163*, 187–198. [[CrossRef](#)] [[PubMed](#)]
36. Parimelazhagan, V.; Jeppu, G.; Rampal, N. Continuous Fixed-Bed Column Studies on Congo Red Dye Adsorption-Desorption Using Free and Immobilized Nelumbo nucifera Leaf Adsorbent. *Polymers* **2021**, *14*, 54. [[CrossRef](#)] [[PubMed](#)]
37. Ben Arfi, R.; Karoui, S.; Mougim, K.; Ghorbal, A. Adsorptive removal of cationic and anionic dyes from aqueous solution by utilizing almond shell as bioadsorbent. *Euro-Mediterr. J. Environ. Integr.* **2017**, *2*, 20. [[CrossRef](#)]
38. Farah, J.Y.; Elgendy, N. Performance, kinetics and equilibrium in biosorption of anionic dye Acid Red 14 by the waste biomass of Saccharomyces cerevisiae as a low-cost biosorbent. *Turk. J. Eng. Environ. Sci.* **2013**, *37*, 146–161.
39. Alhujaily, A.; Yu, H.; Zhang, X.; Ma, F. Adsorptive removal of anionic dyes from aqueous solutions using spent mushroom waste. *Appl. Water Sci.* **2020**, *10*, 183. [[CrossRef](#)]
40. Grabi, H.; Lemlikchi, W.; Derridj, F.; Lemlikchi, S.; Trari, M. Efficient native biosorbent derived from agricultural waste precursor for anionic dye adsorption in synthetic wastewater. *Biomass Convers. Biorefinery* **2021**, 1–18. [[CrossRef](#)]
41. Grabi, H.; Derridj, F.; Lemlikchi, W.; Guénin, E. Studies of the potential of a native natural biosorbent for the elimination of an anionic textile dye Cibacron Blue in aqueous solution. *Sci. Rep.* **2021**, *11*, 9705. [[CrossRef](#)]
42. Banerjee, S.; Dastidar, M. Use of jute processing wastes for treatment of wastewater contaminated with dye and other organics. *Bioresour. Technol.* **2005**, *96*, 1919–1928. [[CrossRef](#)]
43. Mbarki, F.; Kesraoui, A.; Seffen, M.; Ayrault, P. Kinetic, thermodynamic, and adsorption behavior of cationic and anionic dyes onto corn stigmata: Nonlinear and stochastic analyses. *Water Air Soil Pollut.* **2018**, *229*, 95. [[CrossRef](#)]
44. Jin, L.; Li, W.; Xu, Q.; Sun, Q. Amino-functionalized nanocrystalline cellulose as an adsorbent for anionic dyes. *Cellulose* **2015**, *22*, 2443–2456. [[CrossRef](#)]
45. Lyu, W.; Yu, M.; Feng, J.; Yan, W. Highly crystalline polyaniline nanofibers coating with low-cost biomass for easy separation and high efficient removal of anionic dye ARG from aqueous solution. *Appl. Surf. Sci.* **2018**, *458*, 413–424. [[CrossRef](#)]
46. Zhou, T.; Lu, W.; Liu, L.; Zhu, H.; Jiao, Y.; Zhang, S.; Han, R. Effective adsorption of light green anionic dye from solution by CPB modified peanut in column mode. *J. Mol. Liq.* **2015**, *211*, 909–914. [[CrossRef](#)]

47. Su, Y.; Zhao, B.; Xiao, W.; Han, R. Adsorption behavior of light green anionic dye using cationic surfactant-modified wheat straw in batch and column mode. *Environ. Sci. Pollut. Res.* **2013**, *20*, 5558–5568. [[CrossRef](#)] [[PubMed](#)]
48. Oei, B.C.; Ibrahim, S.; Wang, S.; Ang, H.M. Surfactant modified barley straw for removal of acid and reactive dyes from aqueous solution. *Bioresour. Technol.* **2009**, *100*, 4292–4295. [[CrossRef](#)] [[PubMed](#)]
49. Ibrahim, S.; Fatimah, I.; Ang, H.-M.; Wang, S. Adsorption of anionic dyes in aqueous solution using chemically modified barley straw. *Water Sci. Technol.* **2010**, *62*, 1177–1182. [[CrossRef](#)] [[PubMed](#)]
50. Ansari, R.; Seyghali, B.; Mohammad-Khah, A.; Zanjanchi, M.A. Highly efficient adsorption of anionic dyes from aqueous solutions using sawdust modified by cationic surfactant of cetyltrimethylammonium bromide. *J. Surfactants Deterg.* **2012**, *15*, 557–565. [[CrossRef](#)]
51. Namasivayam, C.; Sureshkumar, M. Anionic dye adsorption characteristics of surfactant-modified coir pith, a ‘waste’ lignocellulosic polymer. *J. Appl. Polym. Sci.* **2006**, *100*, 1538–1546. [[CrossRef](#)]
52. Jiang, Z.; Hu, D. Molecular mechanism of anionic dyes adsorption on cationized rice husk cellulose from agricultural wastes. *J. Mol. Liq.* **2019**, *276*, 105–114. [[CrossRef](#)]
53. Koay, Y.S.; Ahamad, I.S.; Nourouzi, M.M.; Abdullah, L.C.; Choong, T.S.Y. Development of novel low-cost quaternized adsorbent from palm oil agriculture waste for reactive dye removal. *BioResources* **2014**, *9*, 66–85. [[CrossRef](#)]
54. Benabbas, K.; Zabat, N.; Hocini, I. Study of the chemical pretreatment of a nonconventional low-cost biosorbent (*Callitriche obtusangula*) for removing an anionic dye from aqueous solution. *Euro-Mediterr. J. Environ. Integr.* **2021**, *6*, 54. [[CrossRef](#)]
55. Noreen, S.; Bhatti, H.N.; Nausheen, S.; Sadaf, S.; Ashfaq, M. Batch and fixed bed adsorption study for the removal of Drimarine Black CL-B dye from aqueous solution using a lignocellulosic waste: A cost affective adsorbent. *Ind. Crops Prod.* **2013**, *50*, 568–579. [[CrossRef](#)]
56. Won, S.W.; Kim, H.-J.; Choi, S.-H.; Chung, B.-W.; Kim, K.-J.; Yun, Y.-S. Performance, kinetics and equilibrium in biosorption of anionic dye Reactive Black 5 by the waste biomass of *Corynebacterium glutamicum* as a low-cost biosorbent. *Chem. Eng. J.* **2006**, *121*, 37–43. [[CrossRef](#)]
57. Saputra, O.A.; Nauqinida, M.; Pujiasih, S.; Kusumaningsih, T.; Pramono, E. Improvement of anionic and cationic dyes removal in aqueous solution by Indonesian agro-waste oil palm empty fruit bunches through silylation approach. *Groundw. Sustain. Dev.* **2021**, *13*, 100570. [[CrossRef](#)]
58. Lin, Q.; Wang, K.; Gao, M.; Bai, Y.; Chen, L.; Ma, H. Effectively removal of cationic and anionic dyes by pH-sensitive amphoteric adsorbent derived from agricultural waste-wheat straw. *J. Taiwan Inst. Chem. Eng.* **2017**, *76*, 65–72. [[CrossRef](#)]
59. Velinov, N.; Radović Vučić, M.; Petrović, M.; Najdanović, S.; Kostić, M.; Mitrović, J.; Bojić, A. The influence of various solvents’ polarity in the synthesis of wood biowaste sorbent: Evaluation of dye sorption. *Biomass Convers. Biorefinery* **2021**, 1–12. [[CrossRef](#)]
60. Ahmaruzzaman, M.; Reza, R.A. Decontamination of cationic and anionic dyes in single and binary mode from aqueous phase by mesoporous pulp waste. *Environ. Prog. Sustain. Energy* **2015**, *34*, 724–735. [[CrossRef](#)]
61. Demiral, H.; Demiral, I.; Karabacakoglu, B.; Tümsük, F. Adsorption of textile dye onto activated carbon prepared from industrial waste by ZnCl<sub>2</sub> activation. *J. Int. Environ. Appl. Sci.* **2008**, *3*, 381–389.
62. Bhomick, P.C.; Spong, A.; Baruah, M.; Pongener, C.; Sinha, D. Pine Cone biomass as an efficient precursor for the synthesis of activated biocarbon for adsorption of anionic dye from aqueous solution: Isotherm, kinetic, thermodynamic and regeneration studies. *Sustain. Chem. Pharm.* **2018**, *10*, 41–49. [[CrossRef](#)]
63. Zhao, B.; Xiao, W.; Shang, Y.; Zhu, H.; Han, R. Adsorption of light green anionic dye using cationic surfactant-modified peanut husk in batch mode. *Arab. J. Chem.* **2017**, *10*, S3595–S3602. [[CrossRef](#)]
64. Velinov, N.; Mitrović, J.; Kostić, M.; Radović, M.; Petrović, M.; Bojić, D.; Bojić, A. Wood residue reuse for a synthesis of lignocellulosic biosorbent: Characterization and application for simultaneous removal of copper (II), Reactive Blue 19 and cyprodinil from water. *Wood Sci. Technol.* **2019**, *53*, 619–647. [[CrossRef](#)]
65. Ma, H.; Li, J.-B.; Liu, W.-W.; Miao, M.; Cheng, B.-J.; Zhu, S.-W. Novel synthesis of a versatile magnetic adsorbent derived from corncob for dye removal. *Bioresour. Technol.* **2015**, *190*, 13–20. [[CrossRef](#)] [[PubMed](#)]
66. Markets and Markets, Activated Carbon Market by Type, Application (Liquid Phase (Water Treatment, Foods & Beverages, Pharmaceutical & Medical), Gas Phase (Industrial, Automotive), and Region (APAC, North America, Europe, Middle East, South America)—Global Forecast to 2026. 2022. Available online: <https://www.marketsandmarkets.com/Market-Reports/activated-carbon-362.html> (accessed on 15 August 2022).
67. Ao, W.; Fu, J.; Mao, X.; Kang, Q.; Ran, C.; Liu, Y.; Zhang, H.; Gao, Z.; Li, J.; Liu, G. Microwave assisted preparation of activated carbon from biomass: A review. *Renew. Sustain. Energy Rev.* **2018**, *92*, 958–979. [[CrossRef](#)]
68. Büchel, K.H.; Moretto, H.-H.; Werner, D. *Industrial Inorganic Chemistry*; John Wiley & Sons: Hoboken, NJ, USA, 2008.
69. Bhatnagar, A.; Hogland, W.; Marques, M.; Sillanpää, M. An overview of the modification methods of activated carbon for its water treatment applications. *Chem. Eng. J.* **2013**, *219*, 499–511. [[CrossRef](#)]
70. Belyaeva, O.; Krasnova, T.; Semenova, S. Effect of modification of granulated activated carbons with ozone on their properties. *Russ. J. Appl. Chem.* **2011**, *84*, 597–601. [[CrossRef](#)]
71. Delamar, M.; Desarmot, G.; Fagebaume, O.; Hitmi, R.; Pinsonc, J.; Savéant, J.-M. Modification of carbon fiber surfaces by electrochemical reduction of aryl diazonium salts: Application to carbon epoxy composites. *Carbon* **1997**, *35*, 801–807. [[CrossRef](#)]
72. García, A.B.; Martínez-Alonso, A.; y Leon, C.A.L.; Tascón, J.M. Modification of the surface properties of an activated carbon by oxygen plasma treatment. *Fuel* **1998**, *77*, 613–624. [[CrossRef](#)]



73. Otake, Y.; Jenkins, R.G. Characterization of oxygen-containing surface complexes created on a microporous carbon by air and nitric acid treatment. *Carbon* **1993**, *31*, 109–121. [[CrossRef](#)]
74. Silva, A.R.; Freire, C.; De Castro, B.; Freitas, M.; Figueiredo, J. Anchoring of a nickel (II) Schiff base complex onto activated carbon mediated by cyanuric chloride. *Microporous Mesoporous Mater.* **2001**, *46*, 211–221. [[CrossRef](#)]
75. Theamwong, N.; Intarabumrung, W.; Sangon, S.; Aintharabunya, S.; Ngernyen, Y.; Hunt, A.J.; Supanchaiyamat, N. Activated carbons from waste *Cassia bakeriana* seed pods as high-performance adsorbents for toxic anionic dye and ciprofloxacin antibiotic remediation. *Bioresour. Technol.* **2021**, *341*, 125832. [[CrossRef](#)]
76. Nayak, A.; Bhushan, B.; Gupta, V.; Sharma, P. Chemically activated carbon from lignocellulosic wastes for heavy metal wastewater remediation: Effect of activation conditions. *J. Colloid Interface Sci.* **2017**, *493*, 228–240. [[CrossRef](#)]
77. Saha, A.; Basak, B.B.; Ponnuchamy, M. Performance of activated carbon derived from *Cymbopogon winterianus* distillation waste for scavenging of aqueous toxic anionic dye Congo red: Comparison with commercial activated carbon. *Sep. Sci. Technol.* **2020**, *55*, 1970–1983. [[CrossRef](#)]
78. Alhogbi, B.G.; Altayeb, S.; Bahaidarah, E.; Zawrah, M.F. Removal of anionic and cationic dyes from wastewater using activated carbon from palm tree fiber waste. *Processes* **2021**, *9*, 416. [[CrossRef](#)]
79. Extross, A.; Wanknis, A.; Tagad, C.; Gedam, V.; Pathak, P. Adsorption of congo red using carbon from leaves and stem of water hyacinth: Equilibrium, kinetics, thermodynamic studies. *Int. J. Environ. Sci. Technol.* **2022**, 1–38. [[CrossRef](#)]
80. Ravenni, G.; Cafaggi, G.; Sárossy, Z.; Nielsen, K.R.; Ahrenfeldt, J.; Henriksen, U. Waste chars from wood gasification and wastewater sludge pyrolysis compared to commercial activated carbon for the removal of cationic and anionic dyes from aqueous solution. *Bioresour. Technol. Rep.* **2020**, *10*, 100421. [[CrossRef](#)]
81. Paredes-Laverde, M.; Salamanca, M.; Diaz-Corrales, J.D.; Flórez, E.; Silva-Agredo, J.; Torres-Palma, R.A. Understanding the removal of an anionic dye in textile wastewaters by adsorption on ZnCl<sub>2</sub> activated carbons from rice and coffee husk wastes: A combined experimental and theoretical study. *J. Environ. Chem. Eng.* **2021**, *9*, 105685. [[CrossRef](#)]
82. Güzel, F.; Saygılı, H.; Saygılı, G.A.; Koyuncu, F. New low-cost nanoporous carbonaceous adsorbent developed from carob (*Ceratonia siliqua*) processing industry waste for the adsorption of anionic textile dye: Characterization, equilibrium and kinetic modeling. *J. Mol. Liq.* **2015**, *206*, 244–255. [[CrossRef](#)]
83. Malik, P.K. Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: A case study of Acid Yellow 36. *Dye. Pigment.* **2003**, *56*, 239–249. [[CrossRef](#)]
84. Zubair, M.; Mu'azu, N.D.; Jarrah, N.; Blaisi, N.I.; Aziz, H.A.; Al-Harhi, M. Adsorption behavior and mechanism of methylene blue, crystal violet, eriochrome black T, and methyl orange dyes onto biochar-derived date palm fronds waste produced at different pyrolysis conditions. *Water Air Soil Pollut.* **2020**, *231*, 240. [[CrossRef](#)]
85. Periyaraman, P.M.; Karan, S.; Ponnusamy, S.K.; Vaidyanathan, V.; Vasanthakumar, S.; Dhanasekaran, A.; Subramanian, S. Adsorption of an anionic dye onto native and chemically modified agricultural waste. *Environ. Eng. Manag. J.* **2019**, *18*, 257–270.
86. Bouhadjra, K.; Lemlikchi, W.; Ferhati, A.; Mignard, S. Enhancing removal efficiency of anionic dye (Cibacron blue) using waste potato peels powder. *Sci. Rep.* **2021**, *11*, 2090. [[CrossRef](#)]
87. Saygılı, H.; Güzel, F.; Önal, Y. Conversion of grape industrial processing waste to activated carbon sorbent and its performance in cationic and anionic dyes adsorption. *J. Clean. Prod.* **2015**, *93*, 84–93. [[CrossRef](#)]
88. Mittal, A.; Mittal, J.; Malviya, A.; Gupta, V. Adsorptive removal of hazardous anionic dye “Congo red” from wastewater using waste materials and recovery by desorption. *J. Colloid Interface Sci.* **2009**, *340*, 16–26. [[CrossRef](#)]
89. Landin-Sandoval, V.; Mendoza-Castillo, D.; Seliem, M.; Mobarak, M.; Villanueva-Mejia, F.; Bonilla-Petriciolet, A.; Navarro-Santos, P.; Reynel-Ávila, H. Physicochemical analysis of multilayer adsorption mechanism of anionic dyes on lignocellulosic biomasses via statistical physics and density functional theory. *J. Mol. Liq.* **2021**, *322*, 114511. [[CrossRef](#)]
90. Demirbas, E.; Nas, M. Batch kinetic and equilibrium studies of adsorption of Reactive Blue 21 by fly ash and sepiolite. *Desalination* **2009**, *243*, 8–21. [[CrossRef](#)]
91. Vadivelan, V.; Kumar, K.V. Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. *J. Colloid Interface Sci.* **2005**, *286*, 90–100. [[CrossRef](#)]
92. Tanzifi, M.; Yarakı, M.T.; Kiadehi, A.D.; Hosseini, S.H.; Olazar, M.; Bharti, A.K.; Agarwal, S.; Gupta, V.K.; Kazemi, A. Adsorption of Amido Black 10B from aqueous solution using polyaniline/SiO<sub>2</sub> nanocomposite: Experimental investigation and artificial neural network modeling. *J. Colloid Interface Sci.* **2018**, *510*, 246–261. [[CrossRef](#)] [[PubMed](#)]
93. Senthil Kumar, P.; Palaniyappan, M.; Priyadharshini, M.; Vignesh, A.; Thanjiappan, A.; Sebastina Anne Fernando, P.; Tanvir Ahmed, R.; Srinath, R. Adsorption of basic dye onto raw and surface-modified agricultural waste. *Environ. Prog. Sustain. Energy* **2014**, *33*, 87–98. [[CrossRef](#)]
94. Iakovleva, E.; Sillanpää, M.; Maydannik, P.; Liu, J.T.; Allen, S.; Albadarin, A.B.; Mangwandi, C. Manufacturing of novel low-cost adsorbent: Co-granulation of limestone and coffee waste. *J. Environ. Manag.* **2017**, *203*, 853–860. [[CrossRef](#)] [[PubMed](#)]
95. Batool, F.; Akbar, J.; Iqbal, S.; Noreen, S.; Bukhari, S.N.A. Study of isothermal, kinetic, and thermodynamic parameters for adsorption of cadmium: An overview of linear and nonlinear approach and error analysis. *Bioinorg. Chem. Appl.* **2018**, *2018*, 3463724. [[CrossRef](#)]
96. Dada, A.O.; Latona, D.F.; Ojediran, O.J.; Nath, O.O. Adsorption of Cu (II) onto bamboo supported manganese (BS-Mn) nanocomposite: Effect of operational parameters, kinetic, isotherms, and thermodynamic studies. *J. Appl. Sci. Environ. Manag.* **2016**, *20*, 409–422. [[CrossRef](#)]

97. Kezerle, A.; Velic, N.; Hasenay, D.; Kovacevic, D. Lignocellulosic materials as dye adsorbents: Adsorption of methylene blue and Congo red on Brewers' spent grain. *Croat. Chem. Acta* **2018**, *91*, 53–65. [[CrossRef](#)]
98. Farzana, N.; Uddin, M.Z.; Haque, M.M.; Haque, A.N.M.A. Dyeability, kinetics and physico-chemical aspects of Bombyx mori muslin silk fabric with bi-functional reactive dyes. *J. Nat. Fibers* **2018**, *17*, 986–1000. [[CrossRef](#)]
99. Haque, A.N.M.A.; Hussain, M.; Smriti, S.A.; Siddiqua, F.; Farzana, N. Kinetic Study of Curcumin on Modal Fabric. *Tekstilec* **2018**, *61*, 27–32. [[CrossRef](#)]
100. Haque, A.N.M.A.; Hussain, M.; Siddiqua, F.; Haque, M.; Islam, G. Adsorption Kinetics of Curcumin on Cotton Fabric. *Tekstilec* **2018**, *61*, 76–81. [[CrossRef](#)]
101. Hubbe, M.A.; Azizian, S.; Douven, S. Implications of apparent pseudo-second-order adsorption kinetics onto cellulosic materials: A review. *BioResources* **2019**, *14*, 7582–7626. [[CrossRef](#)]
102. El-Khaiary, M.I.; Malash, G.F.; Ho, Y.-S. On the use of linearized pseudo-second-order kinetic equations for modeling adsorption systems. *Desalination* **2010**, *257*, 93–101. [[CrossRef](#)]
103. Ho, Y.-S. Second-order kinetic model for the sorption of cadmium onto tree fern: A comparison of linear and non-linear methods. *Water Res.* **2006**, *40*, 119–125. [[CrossRef](#)]
104. Ho, Y.-S. Isotherms for the sorption of lead onto peat: Comparison of linear and non-linear methods. *Pol. J. Environ. Stud.* **2006**, *15*, 81–86.
105. Perez-Ameneiro, M.; Vecino, X.; Cruz, J.; Moldes, A. Wastewater treatment enhancement by applying a lipopeptide biosurfactant to a lignocellulosic biocomposite. *Carbohydr. Polym.* **2015**, *131*, 186–196. [[CrossRef](#)]
106. Islam, G.N.; Ke, G.; Haque, A.N.M.A.; Islam, A. Effect of ultrasound on dyeing of wool fabric with acid dye. *Int. J. Ind. Chem.* **2017**, *8*, 425–431. [[CrossRef](#)]
107. Roy, A.; Adhikari, B.; Majumder, S. Equilibrium, kinetic, and thermodynamic studies of azo dye adsorption from aqueous solution by chemically modified lignocellulosic jute fiber. *Ind. Eng. Chem. Res.* **2013**, *52*, 6502–6512. [[CrossRef](#)]
108. Haque, A.N.M.A.; Farzana, N.; Smriti, S.; Islam, M. Kinetics and thermodynamics of silk dyeing with turmeric extract. *AATCC J. Res.* **2018**, *5*, 8–14. [[CrossRef](#)]
109. Ibrahim, S.M.; Badawy, A.A.; Essawy, H.A. Improvement of dyes removal from aqueous solution by Nanosized cobalt ferrite treated with humic acid during coprecipitation. *J. Nanostructure Chem.* **2019**, *9*, 281–298. [[CrossRef](#)]