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The Use of Inexpensive Sorbents to Remove Dyes from Wastewater - A Review

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HIGHLIGHTS

- The application of inexpensive adsorbents to remove dyes from wastewater was reviewed.
- The various removal technologies, along with their Pros and Cos were highlighted
- Adsorption techniques were found to be very effective in dyes removal.
- Adsorbent from biomass wastes is gaining increasing popularity.
- Aerobic, anaerobic, or mixed processes also proved effective in removing dye.

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ABSTRACT

Dyes are utilized in various industrial applications, and some businesses' effluents include hazardous dyes. Humans, aquatic creatures, and the environment are all harmed by dyes. As a result, adequately treated dyes that manage wastewater must be before being discharged into nearby bodies of water. Adsorption has proven to be high and cost-effective in removing dyes from wastewater. The sorbent material for dye removal from industrial effluent is activated carbon, but its high cost limits massive-scale utilization. The use of cost-effective adsorbents for wastewater discharge dye elimination is discussed and analyzed in this paper. This review underlines and displays a preview of these IASs, including natural, industrial, and made-up materiality/wastes and their utilization in removing dyes. Experiments have shown that various inexpensive non-traditional adsorbents lead to effective dye removal. Accordingly, studies dealing with the search for effective and affordable sources from current resources are becoming increasingly crucial for eliminating dye. The excess desire for functional and affordable processing modes and adsorption significance has led to inexpensive alternative sorbents (IASs). The isotherm analysis and adsorption kinetics indicate that Langmuir / Freundlich, besides the pseudo-second-order model, is the most used pattern for convenient empirical adsorption datum. Low-cost by-products from the agricultural, residential, and industrial sectors have been identified as viable wastewater treatment alternatives. They make it possible to remove contaminants from wastewater while also contributing to waste minimization, recovery, and reuse. This review revealed that some IASs, have ratable adsorption capabilities and rapid kinetics, besides having vastly available.

1. Introduction

While the industrial revolution enhanced human life and health care, it also resulted in environmental degradation, putting the world in grave danger [1]. Because the population has increased and businesses have developed, the need for water purification has increased. Specific industries significantly impact the environment due to the dye-containing effluent they produce [2]. Suppose dyes in wastewater from the textile, food processing, paint, cosmetics, and tanneries industries are not cleaned before being released into aquatic environments. In that case, they represent a substantial source of pollution [3,4].

The dye is a chemical ingredient used to create a colored material that adheres to the substrate. Nowadays, dyes are widely utilized in various sectors, such as rubber, plastic, marine, transportation, and culinary [5,6]. Organic or inorganic dyes are available. Dyes are categorized according to the materials used, chromophore, nuclear structure, and industrial categorization [2]. The textile industry's unavoidable release of hazardous colored effluent during the dyeing process is apparent. Around 10-15% of the dye produced by companies is discharged directly into the environment during the dyeing process, which may negatively affect the ecosystem [7]. Globally, water quality has deteriorated significantly over the last several decades. Such a case was mainly due to the human population's exponential growth, unregulated freshwater use, rapid industrialization, and unplanned urbanization. The removal of dyes from wastewater was reached using Various techniques, including adsorption,

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coagulation and flocculation, membrane filtering, and advanced oxidation [8–11]. Due to their complicated aromatic structure that is reluctant to bacterial dissolution, residual dyes in wastewater effluents complicate conventional treatment techniques.

It can result in brightly colored effluents that have been treated [12]. Recently, adsorption has been hailed as a cost-effective, efficient, and promising method for pollutant removal. It appears to have the highest potential for removing contaminants from the aqueous medium [13].

Due to its high effectiveness, extensive implementation for removing wastewater elements, and ease of applicability, adsorption has gotten a lot of attention. Activated carbon adsorption plays an essential role in contemporary adsorption research because of its vast surface area, rich pore structure, and consistent surface chemical characteristics. However, the applicability of this technology is limited due to complex and expensive preparation operations [10,11]. Thus, Utilizing low-cost, environmentally sustainable raw materials is an appealing feature of investigation [16,17]. Adsorbents for water treatment that are cost-effective and easy to design have been increasingly popular in recent decades [18].

In recent years, adsorbents obtained from natural, agricultural, and industrial wastes have increasingly been employed in place of activated carbon. There are numerous benefits of using trash in wastewater treatment. The most significant benefit is the availability of a different solution to the waste disposal problem. When considering the low cost of adsorbents made from industrial waste, "waste disposal" is an environmentalist method that gives economic benefits. Furthermore, these adsorbents are notable for their significant efficacy and capacity in wastewater treatment [19–21]. The use of cost-effective non-conventional materials to replace synthetic adsorbents is highly relevant in research and development. currently [22].

This review paper focuses on numerous novel adsorbents and their ability to adsorb dyes (implementation of different sustainable, low-cost alternative adsorbents and their maximum adsorption capacity). In addition, the advantages, characteristics, and limitations deal with sorption materials are discussed.

2. Dye Treatment Methods

Wastewater discharge contains artificial dyes that can create an environmental hazard because of the risks of dealing with the environment and wastewater's effect on human health discharge. Various segregation methods have been used for dye separation from Water-based solutions. Separating dyes uses physical, chemical, and biological approaches [23]. The features and limitations of various technologies used for dye elimination from wastewater are summarized in Table 1 [24].

Table 1: The dye removal technology (benefits and drawbacks) [24]

Treatment	Kind	Features	Disadvantages
Chemical	Electrochemical	No sludge production It does not require significant addition of chemicals	Electricity is expensive. In comparison to other remediation, it is less effective
	Coagulation- flocculation	Cost-effective An essential method in textile wastewater treatment	Production concentrated sludge PH dependent
	AOPs	Able to remove the dye in unusual conditions No sludge production Quick reactions	Expensive Forms by-products PH dependent
Physical	Adsorption	Re-generable adsorbent Efficient for a wide variety of dyes Simple and flexible	Costly adsorbents,
	Membrane	So practical and valuable method	Need periodic replacement Membrane fouling
	Ion exchange	High efficiency Low costs Able to regeneration	Not effective against a wide variety of dyes
Biological	Enzyme	Non-toxic Cost-effective Efficient method Reusable	Amount of enzyme generation
	Fungi	Degradability of specific contaminants, such as dyes, is a possibility Friendliness to the environment	It takes a long time for growth
	Yeast	Rapid growth Survive in undesirable environmental conditions	pH-dependent
	Algae	Environmental Friendly Cheap	Unstable system
	Bacteria,	Easy cultivation Grow rapidly Environmental Friendly	pH-dependent

3. Adsorption

The most common technique of dye removal is adsorption [25]. Adsorption is a segregation process in which fluid substances attach to the external and internal solid surfaces of adsorbents materials. The segregation is dependent on adsorbents selectively adsorbing pollutants, in other words, thermodynamic and kinetic selectivity, due to particular interactivity between the adsorbent material's surface and the contaminants that have been adsorbed, molecular diffusion from the liquid to the solid. The wastewater, the adsorbent, and the adsorbate, for instance, the solution synthesized or water effluent, are all engaged in this face phenomenon, resulting from complex interactivity between these elements. It's fair to assume that the interactivity strengths between the three adsorption combinations will influence the adsorption amplitude[26]. Adsorption is a clean water technique that has much potential. A variety of organic and inorganic materials have been utilized for wastewater purification. Heavy metals and dyes, among other contaminants, are particularly important because of their poisonousness. To create a model for removing contaminants from an aqueous medium that is both effective and precise, Thermodynamic and equilibrium data are fundamental specifications [27].

3.1 Role of Adsorbent Characteristics on Adsorption

Characterizing an adsorbent's chemical and physical surface characteristics, such as pore size distribution, specific surface area, particle size, pore volume, and surface functional groups, is critical for adsorption since it allows for predicting an adsorbent's adsorption capacity. Such characteristics are the primary attributes of adsorbent materials that contribute to their adsorption capability and efficiency [28].

As a result, it is essential to have a thorough comprehension of the sorbent properties to determine the affinity of the materials of the sorbent–sorbate for removing organic/inorganic ions. Numerous analytical techniques and equipment are used to depict an adsorbent's physical and chemical surface characteristics, which ultimately determine the material's efficiency as an adsorbent and appropriateness for usage in the adsorption sector [29]. Scanning Electron Microscopy (SEM) is a technique for examining the micro-morphological surface texture of adsorbent materials. It produces high-resolution pictures that allow for a deeper depth of focus on three-dimensional solid samples. Gautam[30] demonstrated the SEM pictures (visible voids and big pores) of inexperienced mustard husk biomass adsorbent for adsorption (Figure 1).

The study of the X-Ray-Diffraction-Spectrum It is critical to examine and measure adsorbent materials' crystalline nature to achieve sufficient adsorption. Powder X-ray diffraction (XRD) is used to assess the crystalline content of adsorbent materials, identify the crystalline phases present, estimate the distance between lattice planes, and investigate the crystallites' epitaxial growth preferred ordering within the material [28]. Lin [31] investigated the removal of anionic and cationic (orange II (ORII) and MO) and (MB) dye using a derived wheat straw (WS), utilizing XRD to determine the effect of the cellulose crystallinity pre-treatment. Two distinct diffraction patterns at about 16° and 22° were identified in all Diffractograms (Figure 2). The latter was sharper for the pretreated wheat straw (WS) than untreated WS, indicating a higher degree of crystallinity in the pretreated fibers responsible for adsorption.

The Dimensions of Particles: The adsorbent's particle size and shape are critical during the adsorption process since the particle size impacts the available surface area for adsorption. Generally, adsorption capacity rises as the specific surface area increases due to the abundance of adsorption sites. Simultaneously, pore size and micro-pore distribution are highly dependent on the adsorbents' composition and the type of raw biomass material used in their production [30]. Additionally, particle size affects a variety of properties of particulate materials. Therefore, it is a valuable indication of essential features such as content homogeneity, dissolution, and, most significantly, the adsorption rates' quality and performance [28].

Analyses of BET Adsorption are fundamentally a phenomenon of the surface. It is dependent on the properties of the adsorbent and adsorbate process conditions. One of the essential properties of an adsorbent is its specific surface area. A more significant surface area can result in a larger pore volume, allowing for more contact between the adsorbate and adsorbent materials, affecting the effectiveness and efficiency of adsorption substantially. The Brunauer–Emmett–Teller (BET) is an equation typically used to determine the particular surface area, abbreviated as BET (surface area). The point of (Zero charges) (PZC) is crucial in physical chemistry related to adsorption. The pH (PZC) value is the pH surface zero charge. The point of the zero-charge concept is utilized better to understand the adsorption mechanism at various pH values. Adsorption of cations is preferable for pH greater than pH (PZC), whereas adsorption of anions is preferable for pH less than pH (PZC) [32], [33].

The elemental percentage composition analysis provides information on the chemical composition (C, H_2 O2, S, and N_2) of an adsorbent, allowing for a better understanding of the role of chemical characteristics in the adsorption process. Fourier-transform-infrared-spectroscopy (FTIR) is used to determine the surface functional groups of the adsorbent. The FTIR spectrum is obtained between 4000 and 400 cm^{-1}. Thus, the surface functional groups' presence, concentration, and composition may positively categorize the functional groups existing in materials that play critical roles in adsorption and capacity [28], [29].

3.2 Activation of Adsorbents

The implementation of wastes or untreated by-products as adsorbents directly can occasionally result in issues related to decreased adsorption capability for anionic contaminants, as in the case of the characteristic of an adsorbent with a similar charge on the surface. In addition, the release of soluble organic compounds found in the raw materials results in secondary pollution [34–36].

Thus, these materials' physical and chemical amendment or activation is required to improve their affinity for dye adsorption from aqueous solutions, affecting adsorbents' adsorption capacity for improved use. The benefits and drawbacks of the existing modification approach in terms of technology are summarized in Table 2.

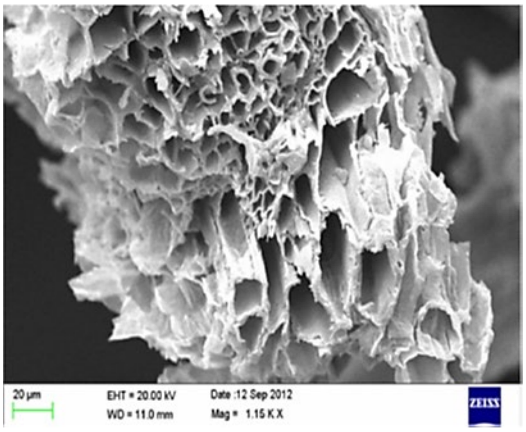

Figure 1: SEM of the raw mustard husk, [30]

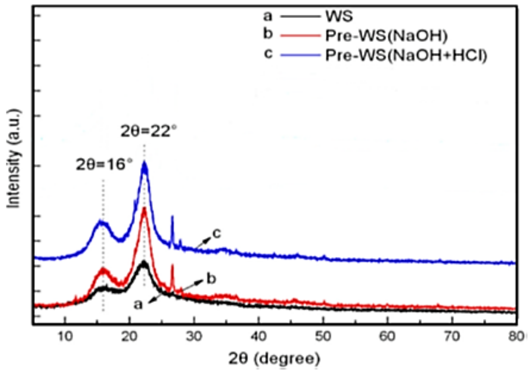

Figure 2: XRD patterns of various WS adsorbents, [31]

3.3 Adsorption Isotherm

Adsorption isothermal models are essential for researching the mechanics and behaviors of adsorption. They can reflect the interactivity between adsorbents and adsorbents [37]. The most classical adsorption models are Langmuir and Freundlich [38], given by equations (1 and 3). Langmuir's exemplary monolayer adsorbed model presupposes that the molecules on the adsorbent surface form a monolayer. Every molecule adsorbed on the surface has the same activation energy for adsorption [39], [40].

$$q_e = \frac{K_L\, q_m\, C_e}{1+K_L\, C_e} \qquad (1)$$

(q_e) (absorption capacity at equilibrium) (mg/g), (q_m) (maximum adsorption capacity) (mg/g),
C_e (concentration of adsorbate at equilibrium) (mg/L), K_L (the adsorption equilibrium constant) (L/mg)

The Langmuir model hypothesis excludes intermolecular interactions, and every adsorption pore or active site can only receive a Single-molecule. Recently, another monolayer adsorption model (Hill model, dubbed Model 2) was created. In contrast to the Langmuir model, the Hill model postulates that every adsorption site may take n molecules [41], [42].

The model can be summarized as follows:

$$Q = \frac{nNm}{1+\left(\frac{C\left(\frac{1}{2}\right)}{C}\right)n} \qquad (2)$$

Q (adsorption capacity at equilibrium) (mg/g), n (the number of molecules connected at each adsorption site), $C_{1/2}$ (half-saturation of adsorbate concentration) (mg/g), (N_m) (the number of adsorption sites that occupied)

The Freundlich isotherm is a well-known adsorption model in multilayers. The assumption depends on the soil, or the water particles are nonlinearly adsorbed adsorbates [43], [44]. In general, the Freundlich model depicts the adsorption behavior of highly interacting species or organic components on materials with high particular surface areas and sophisticated pore structures, such as activated carbon [45]. The model can be summarized as follows:

$$q_e = K_f C_e^{\left(\frac{1}{n}\right)} \qquad (3)$$

q_e (adsorption capacity at equilibrium) (mg/g), Ce (Equilibrium concentration of adsorbate) (mg/L) n (Constant represents the adsorption strength), K f (Capacity).

Adsorption investigations are critical for solid-liquid systems because they establish the adsorbent's interaction with the adsorbate [46]. Due to its technical feasibility, versatility, and process simplicity, adsorption has garnered substantial attention in dye wastewater treatment. As a result, it has been the topic of various research studies, the findings of which are listed in table 3.

The Temkin model considers the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms. The model can be summarized as follows:

$$q_e = \frac{RT}{b}\, ln\, K_T + \frac{RT}{b} lnC_e \qquad (4)$$

Where K_T denotes the equilibrium binding constant (l mol-1), b denotes an adsorption heat constant (J mol-1), R represents the universal gas constant, and T indicates the absolute temperature (K). If the adsorption follows the Temkin model, a plot of qe vs. ln C_e will provide a straight line with a slope equal to RT/b and an intercept equal to RT/b ln K_T from which the constants can be derived [46].

3.4 Adsorption Kinetics

Kinetics of adsorption defines the efficiency of an adsorbent [47]. Numerous models were employed to fit experimental data to identify the adsorption kinetics. These models studied dye adsorption dynamics processes to depict the uptake rate of the solute at the solid-solution interface [48] and manage the adsorbate's residence period and desorption possibilities [47], [49].

The Lagergren equation explained the linear form of the pseudo-first-order model as follows:

$$\ln(q_e - q_t) = \ln(q_e) - K_1 t \quad (5)$$

Where (q_e, q_t) (the amounts of dye adsorbed) (mg/g) on the adsorbents at the equilibrium and time t, k_1 is the adsorption rate constant (min−1). The following equation expresses the pseudo-second-order model's linear form:

$$\frac{t}{q_t} = \frac{1}{k_2}\frac{1}{q_e^2} + \frac{1}{q_e}\,t \quad (6)$$

Where (k_2) is the pseudo-second-order model's rate constant (g.mg-1.min-1). (k_2) and (q_e) were calculated by intercepting a linear plot of t/qt versus t [50]. Adsorption kinetic modeling is used to calculate the rate of adsorption and rate expressions for a particular process [46]. The kinetics of adsorption must be clearly described. The adsorption process consists of three stages. First, the adsorbate is externally mass transferred from the bulk solution to the adsorbent's external surface. After that, the adsorbate's internal diffusion to the sorption sites occurs, followed by the sorption itself. Specific models assume that the rate-limiting phase in the adsorption process is sorption; others consider diffusion. So, relevant data, the models enable the process of adsorption to be elucidated [51].

3.5 Dye removal by adsorption

The adsorption technique has long been used to remove the dye. It is one of the operations often employed for dye elimination and has many uses in wastewater remediation. Adsorption is when a substance gets concentrated from its liquid or gaseous environment at a solid surface. Carbon adsorption has been used in water purgation since ancient times. In 1881, Kayser used the word adsorption to distinguish the accumulation on the surface from intermolecular penetration for the first time. He proposed that the primary characteristic of an adsorption operation is the material buildup on the surface. It is currently common practice to identify between two forms of adsorption. Adsorption refers to physical adsorption when the attraction between adsorbed molecules and the solid surface is material in the environment. The attractive interactions between the adsorbed molecules and the solid surface in Physical-adsorption are typically van-der-Waals forces, which are weak and result in reversible adsorption. The adsorption process is known as chemisorption when the attraction forces are due to chemical bonding. It's tough to get chemisorbed species off a solid surface due to the greater strength of the bonding in chemisorption [60]. While looking for inexpensive adsorbents for eliminating dyes from waste that already existed, for dye removal, activated rice husk was used as a cheap adsorbent [61]. Oualid [62] studied the removal of MB, a basic dye, by cedar sawdust CS and broken brick BB, and he found that adsorption was 60 mg/l by CS and 40 mg/l by BB. For decades, the adsorption technique has been widely utilized to remove dyes from aqueous solutions since it is a simple and successful process. Several researchers have sought to find or build alternate dye adsorption materials. The significant progress is synthesizing and modifying new adsorbents and dye removal via their adsorption capabilities.

Table 2: The existing modification approaches (The benefits and drawbacks), [29] constant of adsorbent) (mmol/g)

Amendment	Treatment	Features	Disadvantages
Chemical Characteristics	Basic	Enhances uptake of organics	Reduce metal ion uptake in particular circumstances
	Acidic	Increased acidic functional groups on the surface of AC improve metal chelation	It may reduce the surface area and pore volume (BET)
	Impregnation of foreign materials,	Enhances the ability of the built-in catalytic oxidation system	It may reduce the surface area, and pore volume (BET)
Physical characteristics	Heat	(BET) surface area and pore volume are both increased.	Reduce oxygen surface, functional groups,
Biological characteristics	Adsorption	Prolongs AC bed life by rapid oxidation of organics by bacteria before they can occupy adsorption sites	Diffusion of adsorbate species may be hampered by thick Biofilms encasing activated carbon.

Table 3: The Adsorption (capability, isotherm, and kinetic model) for dye removal from some research studies

Adsorbent	Adsorbate	Amount of adsorption(mg/g)	Kinetics Model	Adsorption isotherm	Reference
Almond shell activated carbon	Crystal Violet	625	Pseudo second order	Langmuir	[52]
Tea waste	Astrazon Blue FGRL	263.16	-	Freundlich	[53]
Biomass compound of pine, oak, hornbeam, and fir sawdust	Malachite green	48.261	Intraparticle diffusion	Freundlich	[54]
Carbonized Watermelon	Methylene Blue	200	Pseudo second order	Langmuir	[55]
Psyllium seed Power	Reactive Orange 16	206.6	-	Langmuir	[56]
Walnut Shells Power	Methylene Blue	178.9	Pseudo second order	Langmuir	[57]
Banana Peel Powder	Congo Red	164.6	Pseudo second order	Langmuir	[58]
Natural Cocoa shell	Azur II	12.03	Pseudo second order	Langmuir-Freundlich	[59]
plasma-treated Cocoa shell	Azur II	14.04	Pseudo second order	Langmuir-Freundlich	[60]

4. Types of adsorbents utilized for effluent dye elimination

4.1 Activated-carbon AC

Activated-carbon AC is a famous adsorbent with a considerable specific surface area, porous body, and thermos-stability. It is widely used in various applications, including the elimination of contaminants and odors from liquid and gaseous phases, medicinal utilization, catalysis, storing gas, electrode substances in electrochemical appliances, and drinking water. Adsorption on AC has been proven to be a particularly productive technology for wastewater removing colors relating to its ability to efficiently adsorb a wide range of contaminants, rapid adsorption kinetics, cost-effective, and design simplicity. Over the last few years, there has been a surge in interest in AC development for agricultural and industrial waste dyes [63].

4.2 Inexpensive Alternative Sorbents (IASs)

Activated carbon AC presents numerous drawbacks. It is highly costly; the higher the quality, the considerable the cost, non-eclectic and ineffectual against vat dye. The expense of regenerating saturated carbon is also high and complicated, and as a result, the adsorbent is lost. For most contamination dominance implementations, the usage of carbon derived from costly starting materials is also illogical. As a result, many workers are looking for more cost-effective adsorbents. Because of the issues mentioned above, research into developing alternate sorbents as a substitute for costly AC has increased recently. Various natural solid supports that can remove contaminants from impure water at a low cost have received a lot of attention. When evaluating adsorbent materials, their expense is a crucial factor to consider. It might be low-cost if a sorbent requires minor processing, is abundant in nature, or is a waste product or result from another sector. For example, industrial and agricultural waste materials, natural materials, and bio-sorbents are potentially cost-effective sorbent alternatives. Many of them have been tried and are being considered for dye elimination [64].

4.3 Naturalistic materials,

Naturalistic materials exist in nature and are utilized as is or with little treatment as Inexpensive Alternative Sorbents (IASs).

4.3.1 Clay minerals

The successful use of various clay minerals as adsorbents for eliminating various dye types using their sorption qualities (high surface area, the chemistry of surface, lack of toxicity, and potential for ion exchange. Clay minerals are ecologically beneficial due to their properties (basilar, sour, interactive) from wastewater and water as a prospective alternate to AC has only lately attracted extensive solicitude. Clay is a naturally occurring material predominantly formed of accurately grained metals. It may be plastic in the presence of adequate water while it hardens dry or charred. Even though clay contains p-silicates, Other minerals that provide flexibility and hardness may also be involved while dry or burnt [65]. Bentonite can be considered a low-cost adsorbent option and is used as abundant in nature. It has distinct physicochemical characteristics. The capability of bentonite to exchange cations is a significant reason for its use as an adsorbent. Previous research has shown that substituting the natural clay inorganic cations with appropriate quaternary amine cations or a surfactant to eliminate organic contaminants from an aqueous solution might influence the bentonite's capability to exchange [66]. Huang [67] studied the adsorption capability of bentonite for Acid red1 and Rhodamine B (RhB). He found that the pH and concentration influenced the dye's adsorption. Higher pH will generally produce higher adsorption for Acid red1 and RhB. The maximum adsorption amount of Acid red 1 and RhB were157.4 mg/g (pH 8.0) and 173.5 mg/g (pH 9.0), respectively. As a low-cost clay, Naturalistic zeolite can eliminate several cationic dyes such as MB, safranin, malachite green, etc. In contrast, anionic dye adsorption research is sparse [68]. Adsorption Capabilities for some adsorbents are reported in table 4.

4.3.2 Siliceous materials

Mesoporous substances were adsorbents employed within non-ionic, buffered, and saline media for dyes elimination. As electrostatic forces are the leading forces, hydrogen power (pH) significantly impacts the adsorption capability of siliceous compounds. The ionic vigor affects the adsorption capability of siliceous materials, which is six times more in a buffered medium than in nonionic media. On the other hand, Ionic vigor has little effect on dye adsorption on Mesoporous carbon [69]. Siliceous materials can adsorb Various organic contaminants, including dyes, at an affordable rate. Because of their height, amorphous pored and powered, thermic constancy is readily available and exhibits high sorption characteristics due to their extraordinarily high porosity structure and mechanical flexibility [67].

4.4 Biomass Solid-Waste Based Activated Carbon Adsorbent

An effort to build a cost-effective and productive adsorbent alternate to expensive commercial coal-based AC (CAC) is an activated carbon adsorbent generated by modifying and triggering a significant amount of raw biomass. Due to its high adsorption capability is widely utilized in implementations that deal with the protection of the environment to remove gases and liquids pollutants. The internal pore characteristics of AC, such as pore size distribution, surface area, and pore volume, are mainly responsible for their solid adsorptive capabilities. Physical or chemical activation techniques are used in the activation process. Chemical activation has two advantages over physical activation: first, the process can be completed at a lower temperature, and second, the carbon output of chemical activation is often higher. AC gained from Agrarian by-products has the feature of an efficacious low-cost surrogate for non-renewable coal-based granular activated carbon (CACS), providing that they have comparable or preferable adsorption competence. In addition, agrarian by-products are good sources of raw materials for AC manufacture since they are plentiful [29]. Adsorption Capabilities for some adsorbents are reported in table 3.

4.1 Agrarian Solid Wastes

Agrarian solid wastes are affordable and readily available adsorbents for removing contaminants, and they may be suitable potential adsorbents due to their physic-chemical features and depressed cost. Agricultural products are readily available in vast amounts worldwide, resulting in a tremendous amount of waste being rejected. Many investigations of dye adsorption by agricultural solid wastes have been reported, and several adsorbents originating from agricultural solid wastes have been employed for dye removal from wastewater._The Agrarian and industrial sectors are discarded large amounts of untreated waste, contaminating land, water, and air, causing environmental deterioration. On the other hand, improper treatment of this waste causes similar problems. As a result, pollution legislation should be adopted to prevent or reduce the movement of dangerous materials to other places. As a result, numerous proposals have been proposed in the last few years to appropriately dispose of these wastes, such as extensive usage as adsorbents for contaminant removal, particularly for dye removal, where it demonstrated significance. Agrarian wastes are less expensive than other adsorbent materials, eco-friendly, and readily available in large quantities. Agrarian wastes are typically used without or with minimal processing, so they are superior to other adsorbents, avoiding the energy costs of heat, treatment and utilizing a low-cost raw material. Alternative agricultural by-products like peanut hull, coir pith, and rice husk are commonly used as dye adsorbents [128]. Adsorption Capabilities for some adsorbents are reported in table 3.

4.2 Industrial by-Product

Like the power plant, mining, several manufacturers emit large amounts of manufacturing waste. Fly and bottom ash, slag, and other wastes present various disposal challenges. The ideal approach is to repurpose those waste materials for other purposes to address the waste management issues [129]. A variety of depressed cost adsorbents derived from industries of steel and fertilizer wastes in the past were developed and tested to eliminate anionic dye from watery sols [130]. The outcomes show that non-organic wastes are not suitable for removing organic compounds. The batch method was used to investigate dye adsorption in the fertilizer industry. Carbon slurry is subject to liaison duration, concentricity, temperature, and particle volume. According to the Langmuir model, the physical nature and exothermic of the adsorption isotherm were demonstrated. The kinetic datum conforms to Lagergren's equation with good engagement values ranging from 0.9998 to 0.9999, showing that adsorption is a first-order procedure. The researchers studied adsorption on fertilizer industry material compared to AC type. They discovered that the produced adsorbent is around 80% as productive as AC, making it a low-cost option for dye removal from effluents [130]. Adsorption Capabilities for some adsorbents are reported in Table 3.

4.2.1 Metal Hydroxide Sediment MHS

MHS, a type of industrial waste produced by galvanic baths, comprises metals precipitated from effluents after alkalinization. This solid waste contains non-soluble minerals in the format of O/OH, such as Fe, Al, Cr, and Cu, which can be found in this solid waste, posing ecological and validity problems. The severe toxicity of this trash and the rarity of landfills capable of handling category (I) waste fabricate its disposal costly. Furthermore, these materials, which have little commercial value and considerably cause disposal issues, have been investigated as a productive and environmentally friendly alternative. MHS as an adsorbent in the reactive dye elimination from watery solutions is another undiscovered use. In the textile industry's effluent treatment, the use of adsorbents for depressed-cost waste is a complicated process, requiring careful consideration of environmental research [111].

Table 4: Adsorption Capabilities for some adsorbents,

Category	Adsorbent	Pollutants	Adsorption Capability mg/g	Sources
Clays, zeolites, and their composites,	MP	Red RB	1344	[70]
	MP	Yellow GR	1343	[70]
	MP	Blue RN	1286	[70]
	Mesoporous zeolite	B fuchsin	238	[71]
	Mesoporous zeolite	MB	548	[71]
	Mesoporous zeolite	Crystal violet	1217	[71]
	Natural clay (Turkey)	Acid Red 88	1133	[72]
	Montmorillonite/graphene oxide composite	Crystal violet	746	[73]
	Kaolin-based MS	MB	653	[74]
	AOB/ SAC	MB	414	[75]
	Cellulose/clay composite hydrogel	MB	277	[76]
	PCH / SZ	Acid Blue 25	266	[77]
	Zeolite,chitosan composite	MB	199	[78]
	Smectite (RNCs)	BY 28	77	[79]
Chitosan, cyclodextrin, and their composites	Magnetic b-cyclodextrin chitosan nano-particles	MB	2.78	[80]
	Chitosan/surfactant composite	Acid Orange 7	2353	[81]
	Chitosan/surfactant composite	Orange G	1452	[81]
	Magnetic b-cyclodextrin-graphene oxide	Malachite green	990	[82]
	HP-CD/PEG400 modified Fe3O4 nanoparticles	Congo red	1895	[83]
	b-cyclodextrin-based fibers	MB	826	[84]
	Grafted chitosan beads	Reactive Black 5	709	[85]
	Chitosan sponge	Rose Bengal	602	[86]
	Electrospun composite chitosan aerogel	Indigo carmine	565	[87]
	Chitosan/b-cyclodextrin composite	Methyl orange	392	[88]
	Chitosan/graphene oxide composite hydrogel	Methylene blue	350	[89]
	Polyurethane/chitosan foam	Food Red 17	267	[90]
	Sericin/b-cyclodextrin/PVA composite	Methylene blue	261	[91]
	Halloysite-Cyclodextrin Nanosponges	Methylene blue	226	[92]
	Chitosan/PV alcohol,zeolite	Methyl orange	153	[93]
	Chitosan/HCPC	Indigo carmine	118	[94]
	Coir Pith	Crystal Violet	66	[95]
Agrarian solid wastes	Coir Pith	Rhodamine B,	56	[95]
	Rice husk ash	MB	1456	[96]
	Pretreated rice husk	MB	1348	[96]
	Sugarcane bagasse soot	MB	331	[97]
	AAB	Gentian violet	305	[98]
	Untreated coffee residues	Basic B 3G	295	[99]
	Untreated coffee residues	Remazol B RN	179	[99]
	Cotton fiber	CR	175	[100]
	Cotton fiber	MB	113	[100]
	Pistachio shell	Reactive R 238	110	[101]
	Orange peel	Direct Navy Blue 106	108	[102]
	Pine needles	Malachite Green	97	[103]
	Bamboo sawdust	Congo red	91	[104]
	Modified pine sawdust	Methylene blue	84	[105]
	PET carbon	MB	33.4	[106]
Industrial Solid wastes	Activated red mud	CR	7.08	[107]
	Marble dust	MB	16.36	[108]
	PS	RR 120	14.69	[109]
	FS	RR 120	46.81	[109]
	MH sludge	Congo red	3.57	[110]
	LG-IN	NB180	2.76	[111]
	LG-250	NB180	4.09	[111]
	CFA	Reactive black 5	146.2	[112]
	CFA	Reactive red 239	124.8	[112]
	OFA	MB	40	[113]
	Red mud	Congo red	342.57	[114]
	Red mud	MB	6.54	[115]
	Red mud	IC dye	62.6	[116]
	Red mud	Remazol B.B.	27.8	[117]
	Cork AC-3	MB	765.93	[118]
	Cork AC-4	MB	799.02	[118]
	Cork AC-5	MB	798.66	[118]
Biomass solid-waste based activated carbon	D-Biochar	Acid Orange II	448.4	[119]
	MCNCs	CV	2500.0	[120]
	MCNCs	MB	1428.6	[120]
	Rice BBM	Reactive blue 4	218.82	[121]
	Rice BBM	CV	159.24	[121]
	Corn straw	Malachite green	515.77	[122]
	BP Biochar	MB	862	[123]
	MRHC	MB	344	[124]
	MOF composite	MB	197.90	[125]
	FMZ/Nanocomposite	MO	196.07	[126]
Metal oxide nano-composite	FMZ/Nanocomposite	EY	175.43	[126]
	ZnO (nanocomposite)	MO	65.2	[127]
	ZnO (nanocomposite)	AM	75.9	[127]

4.2.2 Fly Ash

Coal is the most commonly utilized fuel for generating thermic energy in many nations. Electricity can also be created using fuel oil, diesel, or natural gas, which are currently used to turn on Iraqi generating stations. Compared to coal fly ash (CFA), fuel oil fly ash (FOFA) has gotten a lot less press for its research. The (FOFA) has a carbonaceous matrix with varying concentrations of plentiful weighty minerals. The type of feeding fuel, coal or petroleum, specified the chemical composition of FA. Aluminum and silicon are more abundant in CFA, good starter materials for geo-polymers, and a good component for regular Portland cement. Minerals such as Cd, Co, V, and Se are abundant in coal-derived FA and Al, Si, Fe, and Ca. (FOFA) has gotten little interest, and published research has focused chiefly on surface characterization and is a carbon-rich compound that contains little aluminum and silicon. According to TCLP and SPLP, (FOFA) is a hazardous residue. This residue needs to be handled with extreme caution. Metals V and Ni were the most plentiful in the (FOFA). (1M HNO_3) removed 52 % of the Ni, and EDX analysis showed the V presence on the FA particles' surface. FA particles are also spheral, as proven by SEM and laser spectroscopy, with an average particle diameter of 70.5 m. As a result, geo-polymers are the optimum application for heavy oil FA. As an energetic weight building material, stable GPs with a high fraction of FA might be used [131].

4.2.3 Red Mud

In Bayer's alumina extraction operation, red mud (RM) is a solid caustic waste or by-product generated when bauxite ore is digested with sodium hydroxide in a concentrated NaOH solution. In 2015, the universal stock of RM waste was expected to be 4 billion tons, growing to about 120 million tons annually. As a result, its management has become a worldwide ecological challenge for environmental preservation. Therefore, the demand for further information in this area has grown more urgent. Although RM is not considered dangerous in many states, its strong alkalinity and tiny particle volume may constitute a substantial ecological menace. At the same time, its rich iron content makes it an intriguing material for environmental rehabilitation. Hurel [132] examined red mud's potential for environmental remediation in various settings. Amended red mud opens up new possibilities for removing mineral ions, non-organic anions, dyes, and acid mine discharge, which is cost-effective wastewater treatment. The use of this material has been demonstrated in the re-vegetation of RM dumping locations and the remediation of mineral-polluted acidic soils. However, little study has been done on its application in the constancy of toxic residues. Leaching and eco-toxicological trials, on the contrary, have demonstrated that red mud has low environmental toxicity, providing a mechanism for the remediation of the polluted medium. However, RM neutralization is advised for secure disposal and implementation irrespective of the ecological environment [132].

4.1 The Metal Oxides MO

Contaminants are a global threat that is rapidly growing in magnitude. Nano-technology's recent advancements have opened up many possibilities for creating desired Nano-materials in treating these contaminants with significant surface/volume ratios and specific surface characteristics. Nano-materials made of oxides, like iron oxide, zinc oxide, titanium dioxide, and the Nano-composites they've created, in particular, have much promise for removing hazardous mineral ions and carbon-hydrogen contaminants from polluted water. These Nano-materials are usually treated for several efficacious combinations to increase catalytic efficiency and longevity. Furthermore, the utilization of magnetic Nano-particles or Nano-composites allows for magnetic separation and reusability (which is not achievable with non-magnetic Nano-particles), both of which are important for practical use. However, research in this area is still in its early stages, and more research is needed to achieve considerable-scale water refining in real life. Transitional mineral oxide Nano-particles, as innovative environmental and power substances, must have excellent properties to be used. Though mineral oxides are mostly crystal-based, better effectiveness of Amorphous phases is also viable to achieve this. Singh, Barick, and Bahadur [133] described adsorption mannerisms and techniques of methyl blue (MB) on metal oxide Nano-particles MONPs (Fe, Co, and Ni, oxides). They show that the amorphousness of transition MONPs (Fe, Co, and Ni) is controlled by a new process, including laser irradiation in a liquid, which can generate superior adsorption capacity for MB. The precept analysis substantiation attributed to Nickel oxide amorphous indicated that to make novel super dye adsorbents by the technology used [134]. Intact MO (Fe, Ti, Zn, Mg, Zr, Al, oxides) and amended MO are two metal oxides adsorbents. Amended MO is split into two categories: 1) MO Nano-composite with (carbon materials, clay/silica, and polymer, and 2) surface amendment (grafting special functional groups, surfactant, doping in metal solutions) [135]. The assessment of the magnetic Fe3O4 nano-particles of the characterization techniques is shown in Table (5).

4.2 Bio-sorbents and microbial biomass

Biological treatment of dye-containing wastewater using aerobic, anaerobic, or mixed processes is widely used because it is reasonably priced and produces no harmful end products. Various micro-organisms, fungi, and algae were utilized to decolorize and mineralize different dyes. Many micro-organisms have been determined to be promising bio-sorbents. They have cheap running costs, non-hazardous regeneration capacity, and contaminant intake capability. Many dye particles, metals, and other contaminants can be used as carbon or nitrogen sources by pure and mixed cultures of bacteria. Bio-sorption does not require nutrients for bacterial cell growth because it is a metabolism-independent method [145].

Table 5: The assessment of the magnetic Fe_3O_4 Nano-particles Characterization techniques

Method	Analyzed	Features properties	Disadvantages	Ref.
FTIR	Chemical bonding and functional group	-Rapid and cheap measurement - Suitable for gas, liquid, bulk and powdered solid samples, and thin films	-A low Sensitivity for nanoscale analysis	[136], [137]
SEM	Shape, size, and dispersion	- SEM image shows the surface structure	-Only for dry samples	[138]
EDX	Chemical elements	- A full elemental spectrum can be obtained in only a few seconds - Can be used in semi-quantitative mode to determine the chemical composition by the peak-height ratio relative to a standard - Can be employed together with other characterization techniques, such as SEM and TEM	- Cannot detect the lightest elements - Less commonly used for actual chemical analysis - Long analysis time	[139]
XRD	Shape, size, and structure	- Well-organized modalities - Direct measurement of size and shapes of an atomic level	- Only for crystalline materials - Only one binding or conformation site is analyzed - Accessibility is lower compared to electron diffraction	[140]
TEM	Shape heterogeneity, size, and dispersion	- Higher spatial resolution than SEM -Direct measurement	- Ultrathin samples are needed -Equipment is expensive	[141]
DLS	Shape size, size distribution, and agglomeration based on hydrodynamic	-Constructive way for rapid and more consistent measurement - Moderate expenses on equipment	- Restricted size determination - Unable to distinguish between Nano-particles with slight differences in diameter - Unable to resolve polydisperse samples precisely	[142], [143]
SQUID	Magnetic Properties	- High sensitivity up to 10^{-8} - Suitable for a thin and single grain Sample with weak magnetic features - The most sensitive devices for analyzing magnetic properties -Applicable for temperature range up to 400K	- Noise sensitive - Complex handling - Time-consuming	[141], [144]
VSM	Magnetic Properties	- High sensitivity up to 10-6 emu - Fully automated - Suitable for liquid or solid phase-in bulk powder, Nano-particle, and thin-film forms of samples.	- Correction Required - Applicable only for small samples	[144]

5. Combined Adsorbent in the Dye Removal

Using a mixture of adsorbents rather than a single adsorbent, according to some research, can dramatically improve dye removal efficiency. According to other studies, combining traditional adsorbents (physical adsorbents) with a biocatalyst (biological adsorbent) yields excellent dye removal results. According to researchers, AC is factually a highly effective dye adsorbing substance, and combining it with an equally productive enzyme (biocatalyst) might improve dye removal even more. A combined adsorbent might potentially help eliminate many dangerous chemicals simultaneously. If the combined adsorbents complement each other, the dye removal efficiency might be higher than any previous record.

Furthermore, compared to single adsorbents, a mixture of adsorbents removes dye quicker. It is also thought that using a combination adsorbent will result in benefits such as extended retention duration and cheaper costs. The reusability factor of combined adsorbents allows for a low total cost when utilizing a mixture of adsorbents. Because individual adsorbents can only be used once, manufacturing expenditures are significantly greater than when mixed adsorbents are synthesized. Manufacturers of mixed adsorbents for wastewater remediation should explore doing so in the future. It's important to remember that the combined adsorbent will effectively eliminate hazardous particles and be cost-effective and produced from readily available raw ingredients. Real industrial cleansed dye effluents, unlike laboratory trials, comprise a combination of chemicals, dye, and other contaminants. When just one dye is evaluated without intervention from additional contaminants, a significant amount of dye elimination is obtained on a laboratory scale. An entirely different result would be achieved if the dyes were combined with other pollutants and then tested. Future studies on this topic should be considered [146].

Table 6: Comparative analysis of the adsorption capability of various kinds of adsorbents for the elimination of MB [5]

Sorbent Kind,	Adsorption Capability, mg/g	Observation
Modified montmorillonite (inorganic-material)	322.6	Cannot be separated easily,
Sewage sludge (Industrial-by-product)	114.9	Non-reusable and toxic,
Mango seed kernel (agriculture-by-product)	142.86	Non-reusable,
H hollow-silica SD (Magnetite-nanoparticles)	≥ 350 #	Can be regenerated and reused,
L-Tyrosine (modified–magnetite-nanoparticles)	333.33	Highly efficient

6. The Conclusions

Literature analysis indicated that dye production and use had increased dramatically over the previous few decades, posing a significant ecological footprint. As previously mentioned, adsorption has a drawback: adsorbents are expensive, as ACs are not cost-friendly substances. Aside from that, regeneration is costly and involves both adsorbent and efficiency loss. As rules tighten, the efficiency and cost of dye treatment methods become increasingly important. It should be noted that some of the substances can be used as adsorbents with little or no preliminary treatment, allowing them to be used at a minimal cost.

There are numerous types of dyes. Their elimination depends on several factors, such as interactions between adsorbate and adsorbent, the functional groups' role in adsorption, and the adsorbate size. Additionally, the dye sorption kinetics and technique on several materials rely on the composition and experiment conditions. The preferable restoration technique is a significant obstacle to cheap sorption and long-range employment. The strength of adsorbents is a critical yardstick that can indicate whether or not an adsorbent is appropriate for use in practice. The dyes' recovery from adsorbents containing pollutants and the concurrent restoration of waste adsorbents for reusing as reduplicated adsorbents is a significant industrial application of adsorption. It may provide significant economic benefits over commercial activated carbon.

Finally, Agrarian wastes are less expensive than other adsorbent materials, eco-friendly, and readily available in large quantities. Agricultural wastes are typically used without or with minimal processing, avoiding the energy costs of heat, treatment, and utilizing a low-cost raw material. Nano-particles are outstanding adsorbents due to several advantages. Table 6 shows the advantages of adsorbents based on magnetite Nano-particles. Compared to industrial by-products, agricultural by-products, and inorganic materials, magnetite adsorbents are incredibly efficient. Its significant recovery and reusability make it one of the most cost-effective adsorbents, so they are superior to other adsorbents. IASs represent a promising green technology.

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Data availability statement

The data that support the findings of this study are available on request from the corresponding author.

Conflicts of interest

The authors declare that there is no conflict of interest.

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