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Phytoremediative adsorption methodologies to decontaminate water from dyes and organic pollutants

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Persistent organic pollutants and dyes cause major problems during ecofriendly wastewater treatment. To overcome this huge problem, several techniques have been considered and in practice for the safe disposal of organic pollutants in recent years; some of them are discussed and compared herein. This review focuses on new trends for wastewater treatment and compares them with certain other techniques alongside their pros and cons; adsorption is considered the safest among them. Adsorbents derived from agri-wastes have good capacity for the removal of these contaminants owing to their great sorption capacity, high reusability, easy operation, etc. Sometimes they need some modifications for the removal of dyes, which are also discussed in this review. This capacity of adsorbents to chelate dye molecules can be affected by factors, such as pH, the concentration of dyes and adsorbents, and temperature of the system. pH has direct influence on the ionization potential and charge on the outer surface of adsorbents. The findings on isotherms, kinetics, and desorption of plant waste-based biomaterials that are safe for the ecosystem and user friendly and are used for hazardous contaminant removal from water are summarized in this review. Finally, conclusions and future perspectives are presented, and some other materials, such as CNTs and MOFs, are also discussed as efficient adsorbents for eliminating dyes from wastewater. Finally, it is predicted that the adsorption of dyes is a more feasible solution for this dye pollution problem.

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1. Introduction

At present, owing to the rapid growth of industries, the provision of clean water and food is a problem across the world. As many countries, especially in South Asia and Africa, including Pakistan, India, Bangladesh, Serbia, and Ethiopia, are shifting towards industrial revolutions, their problem of water pollution is getting worse. Being one of the major contributors in the textile sector, textile-related pollution factors are very common in developing countries, which are the ultimate source of water pollution here. Some of the chief polluting agents discharged from such industries are coloring agents or dyes. These dyes are exclusively used in many other industries, such as leather tanning, paper, and sugar industries.^{1,2} The discharge of colored substances from all such industrial units into water bodies causes severe contamination.³⁻⁵ The increasing water contamination poses a serious threat to human health because of the poor waste water management systems present in these countries.

The origin of the textile industry dates back 4000 years. The process of alcohol production by sugar fermentation and dyeing of cloths are two prominent fields that are known to be antique. The root of fabric dyeing stretches back to the ancient Egyptian civilization in which people were aware of dyeing using insect extracts and some naturally derived pigments, such as indigo. This happened to be in practice until the middle of the last

century. The first synthetic dye was invented in 1856 by William E. Perkin, from the oxidation of aniline.^{6,7} Today, tens of thousands of synthetic dyes are prepared and more than 1000 dyes are available on a commercial scale. Textile industries use a major portion of the synthetic dyes produced.

The use of synthetic dyes has drastically increased in many domains of our daily life and it is continuously increasing with the growth of industries, such as paper, leather, cosmetic, and paint.⁸ About 10 000 diverse types of dying pigments are used in industries. There is a massive annual production of 0.7 million tons of dyeing agents worldwide.⁹ Out of which 3×10^5 tons of dyeing agents are utilized in the textile sector, which makes them the main user of these dyeing stuffs. Therefore, these industries directly contribute to the pollution of water with a production of 7×10^5 tons of colored untreated waste water discharged directly into water bodies annually. A study revealed that almost 2% of dyes are discharged as effluents from the manufacturing sector, 10% of which are discharged from the textile sector.^{10,11} This untreated water coming out of industries and directly dumped into water bodies causes huge distress to the aquatic flora and fauna of the area. This results in reduced sunlight penetration due to the thin layer of dye formed over the water surface. This affects the photosynthetic process of plants, resulting into an imbalanced food chain in the aquatic life cycle and causing a decline in dissolved oxygen of water bodies that makes the water unsuitable for consumption.¹²⁻¹⁴ These



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effluents discharged also affect the process of seed germination if they penetrate the nearby agricultural land, and production declines consequently.^{15,16}

Industries, especially the textile industry being a big culprit, are responsible for this contamination of water because of their bulk contribution to dye pollution, as studies showed that more than 50% of dyes used in these industries get washed off into the drain. This is due to the weak bonding or inadequate dye-fiber attraction. The consumption of this water containing effluents affects the consumer irrespective of whether it is used for a bathing, washing or drinking purpose.¹⁷ It is very important to monitor the concentration of coloring agents or dyes present in water to be consumed, as even 1.0 mg L⁻¹ of dye can be dangerous for human consumption.¹⁸ Moreover, it causes toxicity to the aquatic ecosystem and mutagenic and carcinogenic effects in humans, such as damage to the kidney, liver, brain, central nervous system, and reproductive system has been reported to be caused by contaminated water.¹⁹⁻²¹

Textile dyes widely used in the industry reportedly have various detrimental effects on humans and other living creatures along with the environment, and their discharge into water bodies directly and indirectly affect a wide range of flora and fauna (Table 1).^{22,23} Various natural and synthetic dyes effect negatively at some stage of their degradation cycle, which may be as parent molecule or derived metabolites, being carcinogenic and skin irritant, these dyes lead in destroying human health and also affect other living creature.²⁴⁻²⁷ The life of an average person gets affected by even 1 mg L⁻¹ of dye in water, which is associated with the direct discharge of effluent-containing wastewater into water bodies.^{26,28-30} This affects the level of DO (dissolved oxygen) and light penetration to the life present underneath. Poor light penetration and less dissolved oxygen in water bodies result in the disruption of the aquatic life cycle.^{31,32} Various heavy metals, such as Al, Cu, Pb, Hg, Fe, Co, As, and Zn, are also related to textile dye molecules and responsible for a number of ill effects on human health, including different cancers, dementia, neural toxicity, and organ failure.³³

In recent years, a great shift has been observed towards environmental protection and huge concern was seen regarding the importance of conservation of environment. It is a need of time, or the price will be borne by the upcoming generations, as small quantity of effluents (dyes) can drastically affect the environment, such as water bodies.⁴⁹ Dye contamination is a potential threat; hence, current governments are trying to pay attention to wastewater treatment, and there is still a lot to be done. As we need a constant improvement in the development of effective procedures with promising results, various techniques (Fig. 1) including microbial degradation (aerobic and anaerobic), coagulation, membrane separation, and chemical oxidation are in practice for the removal of dyes, and each of the techniques has its own limitation (summarized in Table 2).⁵⁰ All the above-mentioned techniques are considered effective but are difficult to use and expensive. Moreover, the reasons to get diverted towards biological approaches for environmental protection include inexpensive nature, more effectiveness, lesser amount of sludge production and better environmental-friendliness than the chemical treatments.⁷ Among these practices, adsorption has the advantages of low cost and better effectiveness for effluent removal, which make it desirable.⁵¹

The sorptive removal of contaminants using agricultural wastes is considered more natural and cheaper than adsorbents prepared chemically, as these by-products appear to be quite effective against certain pollutants, such as heavy metals,^{52,53} phenols,^{54,55} gases,⁵⁶ and dyeing agents.⁵⁷⁻⁵⁹ Extensive research has been done to improve the adsorption capacity of natural adsorbents, and various techniques, including chemical and physical activation, *i.e.*, carbonization, are applied. Generally, the Langmuir isotherm is applied to determine the progress of activation. Water coming out of industries is a combination of various effluents, such as heavy metals, salts, dissolved solids, and dyes, and hence, various adsorbents have been applied so far both as untreated and treated with certain activation agents.^{60,61}

Table 1 Detrimental effects of various dyes on life and environment

Textile dye	Dye class	Detrimental effects
Disperse blue 56	Anthraquinone	Aquatic biota and human fitness ³⁴
Disperse blue 291	Azo dye	Apoptosis, DNA destruction ³⁵
Reactive brilliant red	—	Disrupts human protein function ³⁶
Disperse red 1	Azo dye	Destruction of DNA ³⁷
Acid violet 7	—	Lipid degradation, abnormal chromosomal activity, acetylcholine degeneration in mice ³⁸
Disperse orange 1	Azo dye	Micronuclei formation in human lymphocytes ³⁹
Astrazon red	Azo dye	Glutathione levels decline and carboxylesterase rises in <i>Phanerochaete chrysosporium</i> ⁴⁰
Ramazol turquoise blue G-A	Phthalocyanine	Rise of glutathione s-transferase in <i>Xenopus laevis</i> tadpoles ⁴⁰
Cibacron red FN-3G	Double azo	Glutathione s-transferase inhibition in <i>Xenopus laevis</i> ⁴⁰
Benzopurpurin 4B	Azo class	Destroy aquatic biota ⁴¹
Yellow Favina CXL	—	Weak estrogen agonist response ⁴¹
Reactive dyes 3BS	—	Disruption in functionality of liver and gill tissues of <i>Oreochromis niloticus</i> ⁴²
Direct blue 15	—	Mutagenic in nature ⁴³
Disperse blue 291	—	Mutagenic, genetic and cellular toxicity, DNA disruption ⁴⁴
Reactive black 5	—	Declines urease function, reduced ammonification rate in soil ⁴⁵
Tartrazine	Azo dye	Dermatitis, anaphylaxis in nature ^{46,47}
Acid red 13	Azo dye	Damages DNA chain ⁴⁸



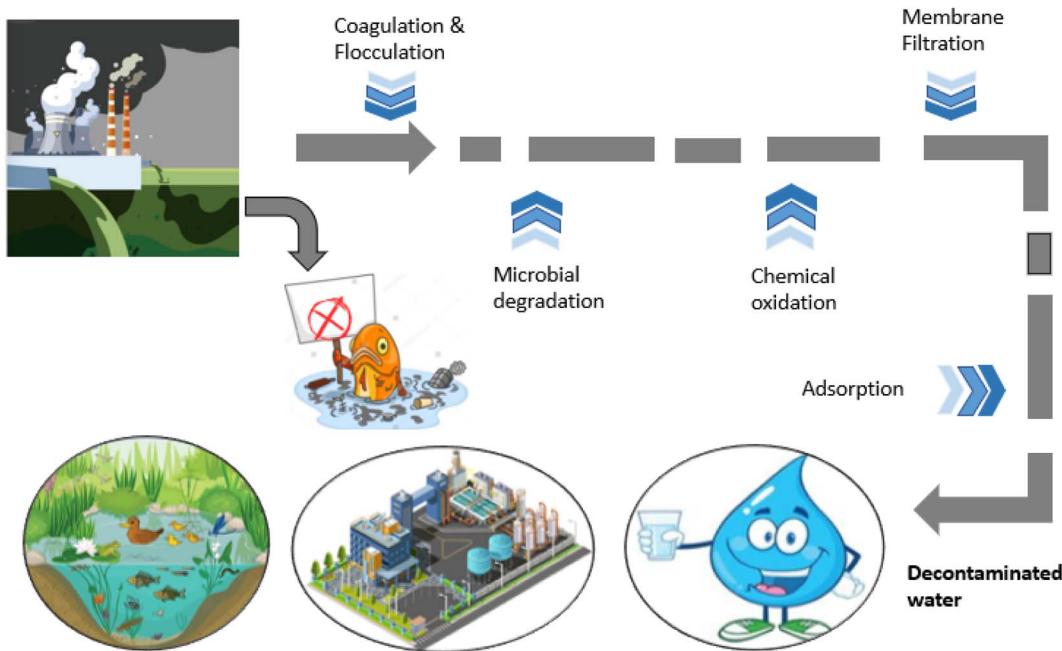


Fig. 1 Multi-steps involved in the removal of contaminants from industrial effluents.

1.1. Classification of dyes

Dye molecules are composed of two essential constituents, namely, chromophore and auxochrome. Chromophore acts as a color producing agent, while auxochrome is responsible for the attraction between dye molecules and fibers.⁶³ Following are some of the major classes of dyes used in textiles: basic dyes, acidic dyes, azo dyes, sulfur dyes, mordant dyes, and vat dyes, among which azo dyes cover a huge ratio of dyes applied (Fig. 2).^{64,65} Dyes can be classified as cationic (basic) dyes and anionic dyes that include acid, reactive, and direct dyes.⁶⁶

1.1.1. Cationic dyes. Cationic dyes are also known as basic dyes and usually dependent on their positive counter parts, *i.e.*, hydrochloride and zinc chloride complexes.⁶⁷ These dyes possess positive functionality and release more positive ions (colored cations) in water. This type of behavior is observed in many types

of dyes, including azo dyes, solvent dyes, numerous polycarbocyclic dyes, and methane dyes. They also include anthraquinone dyes considered as weak and expensive in comparison to azo dyes, which reduce the cost of dyeing.⁶⁸ Basic dyes are preferred, on the basis of their brilliancy and vibrant nature, and these dyes, such as brilliant green and methylene blue, are also utilized as a template for dye removal studies. These dyes are extensively used in silk, nylon, and wool dyeing despite considered harmful.⁶⁶ They are responsible for various medical conditions, such as skin allergies (dermatitis), genetic mutations, and various cancers.⁶⁹ Methylene blue is one of the commonly used basic dyes in textiles, which can be responsible for heart diseases, quadriplegia, tissue necrosis, and digestive tract disorders in humans.⁷⁰ Many different research studies are available, in which agriculture wastes are utilized for the removal of methylene blue

Table 2 Comparison of various techniques in practice⁶²

Technique	Benefits	Drawbacks
Fenton's reagent (oxidation)	Simple implementation	Production of slush
Ozonation (introducing gaseous ozone)	Water volume does not elevate	Brief half-life (nearly 20 min)
Photochemical degradation	Unpleasant smell reduced No slush accumulation	Number of by-products generated
Biological treatments (using living organisms <i>i.e.</i> fungi)	Discoloration of dyes by enzyme production	Release of enzymes uncertain
Membrane separation	Complete dye eradication	Large amount of sludge production
Ion exchange	Complete regeneration of adsorbent	Ineffective for all dye types
Coagulation	Low in cost	Large sludge production
Adsorption (activated carbon)	High efficacy	Economically not feasible
Photodegradation	Non-hazardous, high kinetics of photochemical reaction	Low efficacy, less solar sensitivity
Photo-Fenton/Advance oxidation	Less slush production, effective for high volume	Large Ferrous sludge production
Water splitting	Clear process, economical, use solar energy	Backward reaction, side reaction



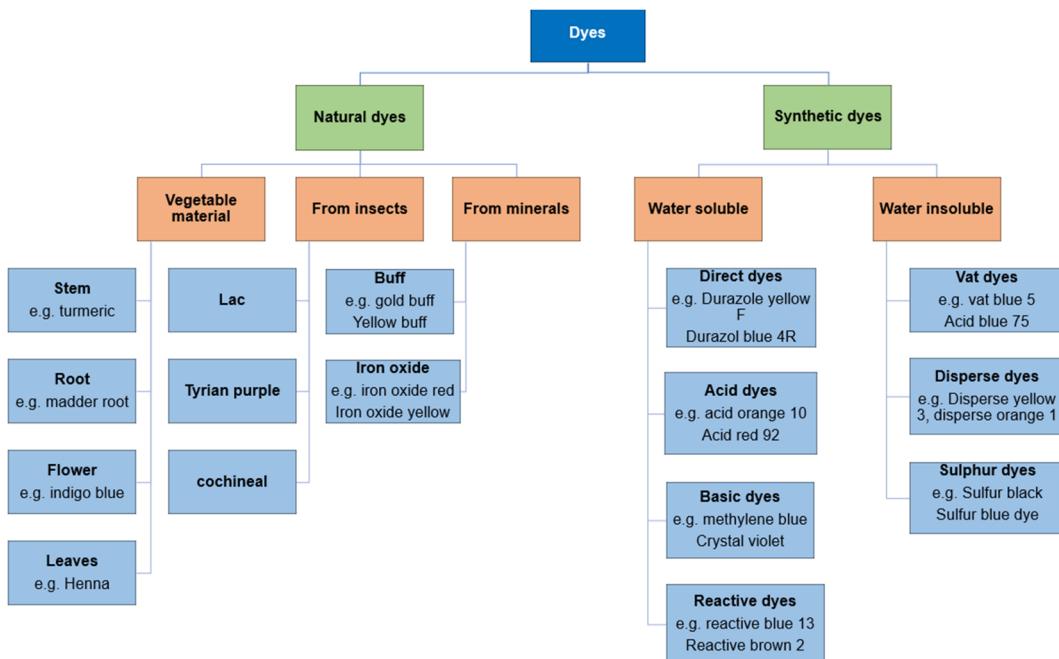


Fig. 2 Classification of dyes according to their origin⁷.

dye from water, for example, coconut shell ($Q_{\max} = 277.9 \text{ mg g}^{-1}$),⁷¹ neem leaf ($Q_{\max} = 351 \text{ mg g}^{-1}$),⁷² guava leaf ($Q_{\max} = 295 \text{ mg g}^{-1}$),⁷³ and peanut husk ($Q_{\max} = 123.5 \text{ mg g}^{-1}$).⁷⁴

1.1.2. Anionic dyes. Anionic dyes are classified based on the production of negative ions, and this group includes a large variety of diverse dyes sharing a common factor of producing negative ions and water solubility, for example, azo, nitro and triphenyl methane dyes. This group also contains numerous reactive dyes.^{67,68} Reactive dyes are generally used in wool and cotton dyeing due to their covalent bonding between the reacting entities and fabrics. These reactive dyes when ejected into the aquatic environment become hazardous due to their efficient hydrolyzing ability and are difficult to be fixed.⁷⁵ Anionic dyes are excessively used in coloring of silk, wool, and synthetic fabrics (polypropylene, polyamide, and modified acrylic fabric). Being effectively soluble in water, these dyes are very efficient for dyeing but have deadly effects on humans owing to their sulfonic nature.⁷⁶ A number of different dye adsorbents have been applied by the researchers for the removal of acid dyes, such as Reactive Yellow 4 (RY4) by apatitic tricalcium phosphate and apatitic octacalcium phosphate,⁷⁷ Brilliant yellow using sepiolite,⁷⁸ Acid black 26, Acid green 25, and Acid blue 7 by pine cone,⁷⁹ and Acid blue 80 by bagasse ash.⁸⁰ Recent developments have been seen inclined towards natural adsorbents, such as agro wastes, *e.g.* mango seed, soy meal, and bamboo, owing to their inexpensiveness and low maintenance.⁸¹⁻⁸³

1.2. Adsorption: an alternative of classical dye elimination procedures

A large diversity of techniques, such as membrane filtration, flotation linked flocculation, ozonation, oxidation, and coagulation, have been employed for the removal of dyes (presented

in Table 2),^{50,84} all of which have drawbacks individually, including slush accumulation, brief life span, huge amounts of side products, and collection of large lumps of sludge.⁸⁵ Adsorption is feasible at both laboratory and industrial levels, being a surface manifestation related to a visible elevation of one component at the boundary of two phases.^{86,87} The adsorption procedure is directly linked to the characteristics of dyeing agents and the surface interaction of the adsorbent depending on its type.⁸⁸ A number of different adsorbents are practically applied in the removal of dyes from waste water and few of them are discussed below and in Fig. 3.

1.2.1. Activated carbon. Activated carbon is extensively used for the removal of dyes from the discharged water. Sources of activated carbon include coal, sawdust, and charcoal, and these are pretreated by fractional oxidation to get a porous

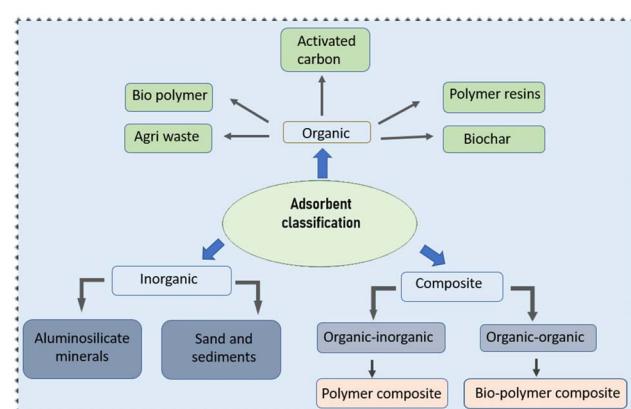


Fig. 3 Classification of adsorbents used for the removal of dyes.



surface that can act as an adsorbent. These activated carbons are of two types: hydrophilic (water loving) and hydrophobic (water repelling).^{89,90} Activated carbon is available in different forms: (a) granular activated carbon (GAC), (b) powdered activated carbon (PAC), and (c) activated carbon tablets, and all these are very effective against effluent removal. GAC is efficient owing to its compliance for the contacting substance and not necessary to remove from a large volume of water. Besides, it showed little intra-particulate interaction. PAC composed of smaller size particles, which are less costly and offers large surface interaction; but the problem with them is their slow diffusion ability and safe removal from wastewater after use.^{91,92} Others like activated carbon tablets are usually obtained from coal and polymeric substances.⁶³ Although this technique is efficient, it is costly and unaffordable for low-resource countries facing water pollution.⁹³

1.2.2. Metal organic frameworks (MOFs). Metal organic frameworks (MOFs), a class of porous materials that are crystalline in nature, are extensively used in the separation of substances, with effective pore size and high surface area (above $6000\text{ m}^2\text{ g}^{-1}$). Multidimensional design, the uniform size of pores, and high surface area make MOFs potential adsorbents for catalysis and chemical separation.^{94,95} MOFs have good capacity of self-assembly, which supports the uptake of relatively large molecules, such as dye molecules. There are several studies in literature of MOFs being used in the removal of dyes, including malachite green, methylene blue, Rhodamine B, xylenol orange, and methyl orange.^{94,96-100}

1.2.3. Nanomaterials and composites. Nanomaterials and composites of various kinds, including metal nanoparticles, carbon nanomaterials (composites and nanotubes), biologically derived nanomaterials, and biochitosan, are widely used in dye removal owing to their better pore volume and surface capacities.¹⁰¹ Nanomaterials (CNTs and carbon nanotubes) show good efficiency in dye removal, but handling them is challenging, which encourages their use in composite forms, such as magnetic nanomaterials, graphene oxides (GOs), and cyclodextrin.¹⁰² Various studies in literature have demonstrated successful dye removal using magnetic nanocomposites, including methylene blue removal with β -cyclodextrin carrying CNTs and Fe_3O_4 nanoparticles carrying CNTs.^{103,104}

1.2.4. Agri solid wastes. Agricultural debris obtained in large quantities every year was found to be very inexpensive, organic in nature, and efficient adsorbents of pollution.¹⁰⁵ This agri-waste is composed of lignocellulosic matter, which is made up of lignin, cellulose, and hemi cellulose. Various adsorbents derived from agricultural waste have been reported previously, which effectively remove dyes from waste water. With increasing effluent or waste water from industries, various methods were applied for their removal to protect the ecosystem.¹⁰⁶ Agricultural wastes are renewable and inexpensive and require no or very little pretreatment and show excellent adsorption capacity for certain dyes.¹⁰⁷

Palm oil has quite a big industrial demand that is directly linked to its production and solid debris produced every year, which can be used in dye removal from waste water. The by-

products include palm shell,¹⁰⁸ palm kernel fiber, and shell.¹⁰⁹⁻¹¹¹ Similarly, coconut is produced almost in the entire of southeast Asia and has been extensively used in adsorption studies in the form of coconut husk,¹¹² coconut sawdust,¹¹³ coconut coir dust,¹⁰⁸ etc.

Apart from that, there are plenty of other agricultural wastes having potential adsorption ability but are rarely used, for example, *Citrullus lanatus* peel (water melon),¹¹⁴ *Psidium guajava* leaves (guava),¹¹⁵ castor seed shell,¹¹⁶ activated lemon peel/sodium alginate composite,¹¹⁷ and activated carbon from kiwi, cucumber, and potato peel.¹¹⁸

1.3. Modification/synthesis of adsorbents

The performance and efficacy of an adsorbent are characterized by factors, such as (a) large surface area, (b) high penetrability with small-sized pores, (c) thermal and chemical stability, and (d) good mechanical strength.¹¹⁹ All these factors play positively towards the efficiency of adsorbents. Certain surface modification techniques are also in practice related to the enhancement of the adsorption capacity of adsorbent materials that revise the physical, biological, and chemical behaviors of substances (Fig. 4).¹²⁰ Adsorbent characteristics get enhanced by modifying the surface charge, roughness, surface area, and porosity, and these modifications are carried out by thermal, chemical, or mechanical procedures. Physical modification treatments favor enhancing the porosity, density, and solubility, while chemical treatments (involving alkali, acid, salt etc.) help in increasing the surface area.^{121,122} Among the physical and chemical modification techniques, chemical treatment gives better results, as it directly influences the surface of adsorbents and not time-consuming along with some additional surface

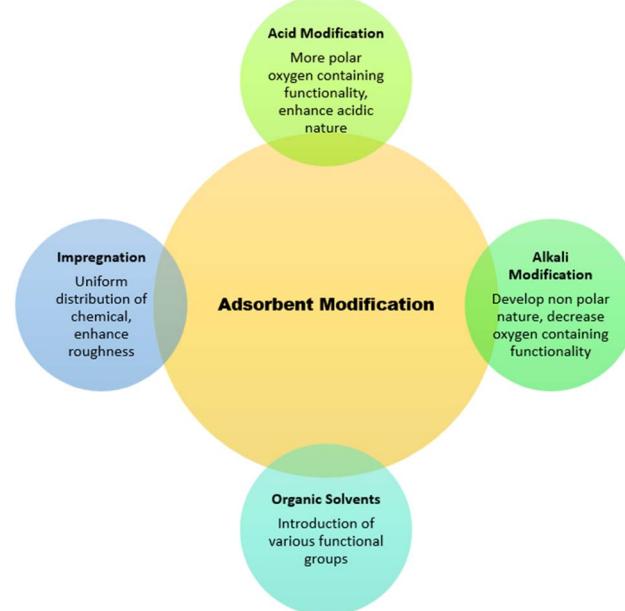


Fig. 4 Types of modification methods of adsorbents and their effects on properties.



characteristics. These modifications can convert a low-cost raw material into an efficient adsorbent.^{123,124}

1.3.1. Acid treatment. The use of mineral acids and oxidizing agents, such as HCl, H₃PO₄, H₂O₂, and HNO₃, for improving the adsorbent behavior of materials is termed as acid treatment or wet oxidation modification.¹²⁵ This treatment enhances the hydrophilic quality and acidic surface of adsorbents due to the reduction of mineral matter present.¹²⁶ It increases the porosity of surface by increasing polar O containing functional moieties, such as carbonyl, carboxyl, and lactone. Moreover, the accumulation of H⁺ on the adsorbent surface promotes the uptake of negatively charged effluents.^{127,128} The modification of brown algae by H₂SO₄ leads to the formation of cylindrical porous structures on the adsorbent surface due to release of trapped gases and the porosity of the adsorbent enhanced, resulting in better adsorption ability.¹²⁹

1.3.2. Alkali treatment. The introduction of reducing agents, such as LiOH, KOH, and NaOH oxides, increases the non-polar nature of the adsorbent surface. The distribution of negatively charged particles on the surface of adsorbent results in better uptake of Toluidine Blue dye on alkali-treated fuller's earth surface.¹³⁰ The alkali (NaOH) treatment of activated carbon results in better pore volume and enhanced surface area, which is caused by the reduction of O-containing functional moieties.¹³¹

1.3.3. Impregnation. The process of uniform dispersion of chemical substances, such as metals, carbonates, and chlorides, onto the porous adsorbent material is termed impregnation.¹²¹ Impregnation elevates the practicality in terms of stability, adsorption ability, and regeneration of

adsorbents. Rehman *et al.*, presented that Zr-impregnated activated carbon showed better porosity, thermal stability, and O functionality.¹²⁶

1.3.4. Organic solvents. Organic solvents, such as alcohols, can be utilized to enhance the adsorption ability and introduction of some more functional moieties. However, owing to the unstable nature and high cost, organic solvents have limited applications in the adsorption process.¹³²

A number of other chemical substances are used in the modification of adsorbents other than those mentioned above, which include neutral solutions and oxidants. Wood biochar modified by KMnO₄ resulted in a more oxygen-containing porous surface coated with MnO_x and showed better uptake of Pb(II), Cd(II), and Cu(II).¹³³

2. Characterization of adsorbents

The characterization of adsorbents shows a number of key features to be considered, including pore size, particle size, pore volume, and morphology. These key factors are directly related to the basic physical properties and behavior of adsorbent materials and are usually characterized using BET, XRD, TEM, and SEM analyses, *etc.*

2.1. Surface area

As the surface area plays a fundamental role in the adsorption efficiency of adsorbents, it is characterized by BET analysis.¹³⁴⁻¹³⁸ The properties of adsorbents significantly depend on the materials used and modification methods applied for production. Activated carbon analyzed with BET may exhibit a surface area of 2630 m⁻² g⁻¹, and similarly, the

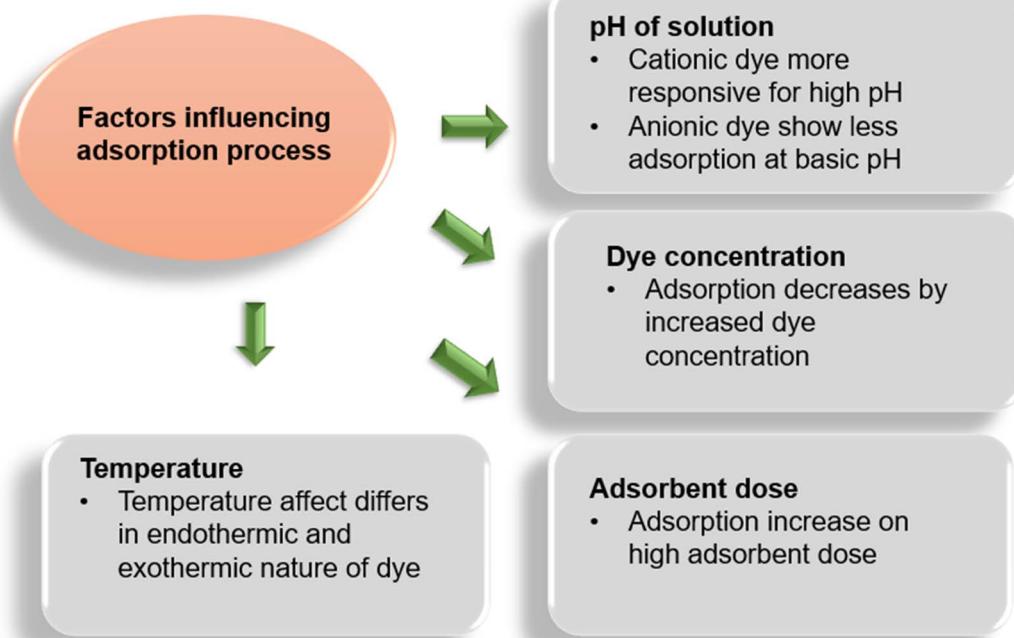


Fig. 5 Influencing parameters of the adsorption process.



pore volume may vary up to $1.91 \text{ m}^3 \text{ g}^{-1}$.^{139,140} However, zeolites may show a surface area around $2300 \text{ m}^2 \text{ g}^{-1}$ with a high proportion of micropores.^{141,142}

Carbon nanotubes and graphene adsorbents show relatively high consideration based on their modification abilities and more surface area as $1000 \text{ m}^2 \text{ g}^{-1}$ based on the composite type and preparation method.^{143,144} Unlike all these adsorbents, the above-mentioned polymeric adsorbents present a smaller pore size based on the polymerization conditions applied. The pore size is inversely proportional to surface area, still it favors the passage of adsorbates onto adsorbents.¹⁴⁵

2.2. Morphology

The morphology, crystal structure, and topography of the adsorbent material are key features in adsorbate uptake onto the adsorbent and are characterized using scanning electron microscopy (SEM), a technique exclusively applied to determine the microstructure of materials.¹⁴⁶ Adsorbents with both micro and mesoporous structures can be visualized by SEM images along with the change in the morphology of adsorbents with any type of chemical or physical treatment and adsorbates loaded in the adsorption/desorption cycle validating the stability of adsorbents. CNTs, MOFs, minerals, biomass, and other synthetic adsorbents can be studied morphologically using SEM and this morphology contributes to the designing of the mode and mechanism of adsorbate uptake.¹⁴⁶⁻¹⁴⁹

2.3. Particle size

The size, shape, and cluster formation of particles help in understanding the behavior of adsorbent materials in adsorbate solutions and approaches to get them separated, especially materials with layered arrangement, such as kaolinite.¹⁵⁰ This characteristic is effectively studied using TEM analysis, describing the shape and size of the particles and the cluster formation of adsorbents and their distribution on solid beds.¹⁵¹⁻¹⁵⁴ Smaller sized adsorbents, such as nanocomposites and graphene-derived adsorbents can be monitored before and after any treatment to determine the defects and other changes associated with layering, particle size, shapes of molecules, and cluster formation.¹⁴³

3. Parameters affecting dye removal

3.1. Effect of solution pH

The acidity or basicity of a solution is termed the pH of the solution. The pH of a solution has great influence on the adsorption process by controlling the degree of electrostatic charge produced by the ionization of dye particles. This, in turn, controls the adsorption rate of dyes.¹⁵⁵ The pH influence on the adsorption process is studied by introducing a known amount of adsorbent and dye within the fixed range of pH attained by adding NaOH (1 M) or HCl (1 M) solutions. Normally, an increasing adsorption trend is observed for the

Table 3 Illustration of linear forms of various isotherm models along with their application in water-soluble dye removal

Isotherm	Equation (linear)	Dye removed	Ref.
Henry	$q_e = K_{\text{HE}}C_e$	Acid yellow 194 Acid red 357 Acid black no. Malachite green Methylene blue Brilliant green	186-188
Langmuir isotherm	$\frac{C_e}{q_e} = q_{\text{max}} \frac{q_e}{K_L C_e}$		114 and 189
Freundlich isotherm	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	Fluorescein Eosin	114 and 189
Dubinin–Radushkevich	$\ln q_e = q_s - K\varepsilon^2$	Methyl orange Malachite green	190 and 191
Temkin	$q_e = \frac{RT}{K_T} \ln A_T + \left(\frac{RT}{K_T} \right) \ln C_e$	Methyl orange Remazol brilliant blue R Methylene blue	188, 190 and 192
Flory–Huggins	$\log \frac{\theta}{C_0} = \log K_{FH} + n_{FH} \log(1 - \theta)$	Remazol brilliant blue R Malachite green Methylene blue	188, 192 and 193
Hills	$\log \frac{q_e}{q_{SH} - q_e} = n_H \log C_e - K_D$	Methylene blue Crystal violet	188 and 194
Halsey	$\log q_e = (1/n_H) \ln K_H - (1/n_H) \ln C_e$	Methylene blue Crystal violet Malachite green	195 and 196
Jovanovich	$\ln q_e = \ln q_{\text{max}} - K_j C_e$	Methylene blue Erichrom black T	188 and 197
BET	$\frac{C_e}{q_e(C_s - C_e)} = \frac{1}{q_m \cdot C_{\text{BET}}} + \frac{C_{\text{BET}} - 1}{q_{\text{max}} \cdot C_{\text{BET}}} \cdot \frac{C_e}{C_s}$	Basic blue 9 Acid blue 29 Acid red 91 Disperse red 1 Basic blue	198 and 199



adsorption of cationic dyes with an elevation in pH. Similarly, a decline in the percentage dye removal for anionic dyes is witnessed and *vice versa*. This phenomenon is strengthened as the positive potential of the solution decreases with the increase in pH and the surface of adsorbents tends to be negative and more supportive towards cationic dye molecules to be carried.¹⁵⁶ While at a low pH, the negative potential of the adsorbent declines and the positive interface improves anionic dye adsorption. Extensive research has been carried out on dye behavior towards the pH change of the solution, *i.e.* reactive black 5 at sunflower seed shell (adsorbed minimum at 4 pH),^{157–160} Gemazol turquoise blue-G at sugar beet pulp (adsorption noticed zero at 6 pH),¹⁶¹ methylene blue (MB) dye at banana stalk (adsorption max. at 4 min at 2 pH),¹⁶² etc.

Adsorption capacity and active points on the adsorbent surface are determined by the linear span of pH sensitivity, which is termed pH_{pzc} (point of zero charge) or pH_{IEP} (iso electronic point).¹⁶³ To study the behavior of adsorbents coming from agricultural sources, iso-electronic point has been investigated by many researchers. Cationic dyes have more favorable adsorption condition, where the pH_{pzc} ranges more towards acidic side, as the surface becomes negatively charged, while the basic side of pH_{pzc} range favors anionic dye adsorption.^{164,165}

The pH_{pzc} is found by taking a range of fixed initial pH values having a known amount of adsorbent added, kept on shaking until equilibrium and the final pH is noted. A graph between $pH_{initial}$ and pH_{final} gives a point where $pH_{initial} = pH_{final}$ considered as an iso electronic point.¹⁶⁶

3.2. Effect of dye concentration

The percentage removal of dyes is directly associated with the initial amount of dye introduced. To determine the impact of initial dye concentration, solutions containing a known concentration of adsorbent were introduced with different doses of dyes and were shaken until equilibrium is attained. The initial concentration of dye introduced is directly related to the availability of binding sites on the surface of adsorbents. Normally, a descending pattern is observed as the concentration of dye introduced initially increased that is linked to the number of binding sites occupied with dye molecules.¹⁶⁷ It is said that the lower the concentration of dye molecules the higher will be the active sites of adsorbents available; however, it favors the loading ability of the adsorbent, which increases induced by the mass transport of dye molecules.^{72,168} Garg *et al.*¹⁶⁹ suggested that the unit adsorption of methylene blue (MB) on sulfuric acid-modified sawdust increased when the MB concentration was increased (50 mg L⁻¹ to 250 mg L⁻¹) under optimized conditions, while a decline in percentage adsorption was also observed. Previous literature affirms the statement that both anionic and cationic dyes show decreased adsorption whenever the dye concentration increases in the solution. As the actual industrial waste water possesses more dye concentrations than that is mentioned in literature, researchers work on empirical schemes founded on equilibrium adsorption

conditions (given in Fig. 5) to calculate the size and the functioning of adsorbent materials. These empirical schemes are of two types: one-step design and two-step design; it was observed that few dyes took more adsorption time for similar adsorption capacity in the one-stage design, while they are more efficient in the two-stage design. This also reduces the process cost.^{169–171}

3.3. Effect of the adsorbent dose

The impact of variable dose concentration is determined by taking adsorbate solutions under optimal conditions with different concentrations of adsorbents and shaken till equilibrium. Generally, an ascending trend in dye removal is seen with the increase in adsorbent dose, which affects dye uptake positively.¹⁷² Studying the impact of dose change helps in determining the ability and efficacy of the adsorbent used, which eventually helps in economic perspective. Literature also supports the fact that the dose increase has positive effects on dye removal and *vice versa* for both cationic and anionic types of dyes.^{173–175}

3.4. Effect of temperature

The influence of temperature on the adsorption of dye is determined by shaking the adsorbent–adsorbate solutions while keeping the other factors constant at different temperatures till the equilibrium is reached. The temperature indicates the nature of dye material, if the adsorption ability of adsorbents elevates with the elevating temperature, then the dye is considered as endothermic because this increase on dye uptake is referred to as increased kinetic energy of the molecules and increased availability of active sites of adsorbents and *vice versa*.^{176,177} Sometimes adsorption capacity may decrease with the increase in temperature that depends on the class of dye. As interacting forces between dye particles and the binding sites may decrease with the increase in temperature.^{109,178,179} A study carried out by Senthilkumaar *et al.*¹⁷⁶ showed that the adsorption ability of activated carbons (by H₂SO₄ and H₃PO₄) from male coconut flowers increases by elevating the temperature. Similar results were found by studies of methylene blue, malachite green, and crystal violet with apricot¹⁸⁰ and methylene blue with garlic peel.¹⁸¹ The class of dye also plays an important role along with temperature, as studies showed that cationic dyes show endothermic nature while anionic dyes depict the exothermic behavior, *e.g.* 4-bromoanilineazo-1,8-dihydronaphthalene-3,6-di-sodium sulphate (BDH) showed exothermic behavior on adsorption with palm kernels. This behavior is explained as increasing temperature may subside the attraction between the binding sites of adsorbents and the dye particles existing in the adsorbed state.¹⁰⁹

4. Adsorption isotherms

To study the adsorption ability and the behavior of adsorbates towards adsorbents, few isothermal studies are summarized in Table 3. These models help in determining the type of surface phase, *i.e.*, mono layer or multilayer. One of the famous isotherm models is the Langmuir isothermal model (eqn (1)),



which is based on the homogenous type of adsorption mechanism. It demonstrates that the single layer of adsorbate attached at a time to the adsorbent surface.^{86,182} Following eqn (1) is the mathematical expression for this model:

$$q_e = \frac{q_{\max} \cdot K_L C_e}{1 + K_L C_e} \quad (1)$$

q_e (mg g⁻¹) is the adsorbate concentration at equilibrium, q_{\max} (mg g⁻¹) is the maximum adsorption capacity, and C_e (mg L⁻¹) is the equilibrium concentration of adsorbate and K_L (L mg⁻¹) is the Langmuir constant.

Usually, the cationic class of dyes demonstrates more adsorption ability than that of anionic class, and this refers to the presence of carboxylate moieties in most agri-wastes used as adsorbents. This functionality supports cationic dyes to be adsorbed, while it suppresses the anionic dye molecules to be adsorbed.¹⁵⁹ Between the acid blue (anionic dye) and basic yellow (cationic dye) dyes adsorbed on coffee waste, the latter showed better adsorption behavior than that of the former.¹⁸³ Some other isotherm models include Freundlich and Temkin isotherms, each having its own contribution towards the understanding of adsorption behaviors. The Freundlich model explains that the multilayer adsorption of adsorbates on the rough surface of adsorbents depicts non-ideal adsorption nature.¹⁸⁴ The Temkin model explains the adsorption behavior and its link with sorption energy, which explains that the heat of adsorption decreases in a linear fashion with the increasing rate of adsorption. In other words, thermal diffusivity declines as more of the active binding sites got covered by adsorbate.¹⁸⁵

Altenor *et al.*²⁰⁰ conducted a study on the removal of methylene blue by vetiver roots (modified physically with carbonization and chemical modification was done by H₃PO₄). Four isotherm studies, namely, Freundlich, Langmuir, Redlich-Peterson, and Brouers-Sotolongo, were carried. Out of all these, the results were

found best aligned with the Brouers-Sotolongo and Redlich-Peterson models, which also found that chemically modified samples showed better adsorption ability towards MB than that of physically modified ones. It shows more alignment with the Langmuir and Brouers-Sotolongo models with adsorption capacities of 423 mg g⁻¹ and 444 mg g⁻¹, respectively. Table 4 presents the list of other research studies made accordingly.

5. Thermodynamic studies

The heat changes and their effects on the overall adsorption process are classified in this section and summarized in Table 5. It presents the effect of temperature, resulting in evident changes in the kinetic energy of the molecules involved in the process. The elevated temperature usually increases the diffusion of dye molecules into the ligno-cellulosic arrangement of adsorbents. Parameters, such as ΔH^0 (enthalpy), ΔS^0 (entropy of the system), and ΔG^0 (Gibb's free energy) (eqn (2)) present the heat changes responsible for the allocation of the exothermic (-ve ΔG^0) or endothermic (+ve ΔG^0) nature of reaction, which also describes the spontaneity of the process.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (2)$$

6. Kinetic studies

The refinement of adsorption process is reviewed by the kinetic studies of adsorption regarding rate constants.²¹³ On the basis of adsorption capacity, the rate of adsorption plays a role in better selection of materials used as adsorbents. Generally, the pseudo-first-order and pseudo-second-order models are used for studying rate kinetics. The pseudo-first-order model generally does

Table 4 Summary of adsorption of dyes by various agricultural wastes

Adsorbent	Dye/adsorbate	pH	Time (min)	Temp (°C)	Best fitting isotherm	Kinetic modelling	Maximum adsorption capacity (q_{\max})	Ref.
Bamboo dust carbon	Methylene blue	—	35	30	Langmuir isotherm	Pseudo first order	143.20	72
Wheat shells	Methylene blue	5–9	60	30	Langmuir isotherm	Pseudo second order	21.50	168
Waste apricot-based activated carbon	Malachite green	—	—	50	Langmuir isotherm	—	163.9	195
Pineapple stem	Methylene blue	10	4	30	Langmuir isotherm	Pseudo second order	119.05	168
Rice husk	Methylene blue	8	40	30	Langmuir isotherm	Pseudo second order	40.50	71
Jujuba seeds	Congo red	2	—	60	Langmuir isotherm	Pseudo second order	55.56	201
Cucumber peel	Orange G	2	250	—	Langmuir isotherm	Elovich model, pseudo second order model	40.5	202
Wheat straw	Orange II	2	—	30	Langmuir isotherm	Pseudo second order	506	203
Palm kernel	BTH4-(bromoaniline-azo-1,8-dihydronaphthalene-3,6-disodiumsulphate)	—	—	23	Langmuir isotherm	—	38.6	109
Polypyrrole/chitosan composites (PPy/Ch)	Acetid orange-RL	4	60	30	Langmuir, Freundlich isotherm	Pseudo first order, pseudo second order	76.9	204
Chitosan-aniline	Crystal violet	>7	60	50	Freundlich isotherm	Pseudo second order	100.6	205
CaO-biochar composite	Phosphates from aqueous solution	11	—	44 (318 K)	Langmuir isotherm	Pseudo second order	240	206



Table 5 Comparative data on the thermodynamics of dye (effluents) removal by agri-wastes

Adsorbent	Adsorbate	Temp. (K)	ΔG^0 (kJ mol ⁻¹)	ΔH^0 (kJ mol ⁻¹)	ΔS^0 (kJ mol ⁻¹ K ⁻¹)	Reference
Orange peel	Methylene blue	298	-7.65	14.8	0.07	207
		308	-8.24			
		318	-9.16			
Potato husk	Crystal violet	293	-20.36	-3.31	-0.009	208
		303	-20.67			
		313	-21.75			
Garlic peel	DR12B	298	-95.39	54.45	0.214	209
		308	-111.2			
		318	-130.1			
Cucumber peel	Methylene blue	328	-160.9			
		293	-4.51	-21.50	-0.059	210
		303	-3.50			
		313	-3.29			
		323	-2.30			
Banana peel	Methylene blue	333	-2.21			
		303	0.12	2.95	0.04	211
		313	-0.36			
		323	-0.83			
Cactus fruit peel	Brilliant green	303	-1.31			
		293	-3.26	-25.43	-0.07	212
		313	-2.54			
Phosphoric acid activated lemon peel	Methylene blue	283	-23.85	-41.84	-63.55	117
		293	-23.22			
		303	-22.58			
		313	-21.98			
Activated carbon from kiwi peel	Methylene blue	298	-20.34	43.62	0.214	118
		308	-22.49			
		318	-24.64			

not go well with real-time data due to adsorption at constant time factor and diverges from the theoretical concept. Hence, the pseudo-second-order kinetic model is used, established on the adsorption ability of adsorbents (solid phase) and suggests the rate-determining step as the chemisorption process.^{214,215} Linear equations for pseudo-first-order (eqn (3)) and pseudo-second-order (eqn (4)) are presented as follows:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \quad (4)$$

q_t (mg g⁻¹) is the adsorbate concentration adsorbed at time t , q_e (mg g⁻¹) is the adsorbate concentration adsorbed at equilibrium, K_1 (1/min) is the rate constant of pseudo-first-order adsorption, K_2 (g mg⁻¹ min⁻¹) is the rate constant of pseudo-second-order adsorption.

Generally, the value of R^2 (regression correlation coefficient) assists in determining the best fitting kinetic model. The studies revealed that the pseudo-second-order model is more likely to be followed for the adsorption of anionic and cationic dyes mostly (Table 3). Extensive research has been made on the adsorption of methylene blue using various natural adsorbents where it was confirmed that they all have a value of R^2 greater than that of the pseudo-second-order model, proving more likelihood for the pseudo-second-order kinetics.^{168,175,216}

7. Mechanism of dye removal

The sorptive removal of dyes from contaminated water over a porous surface may adopt various adsorption mechanisms. The uptake of effluents (dyes) onto the adsorbent surface is driven by a number of interactions, including electrostatic interaction, van der Waals interaction, H-bonding, hydrophobic interaction, and $\pi-\pi$ interactions, as shown in Fig. 6. The sorption of two anionic dyes, namely, congo red and methyl orange on GO-NiFe-LDH has been achieved by both ion exchange (exchange of ions between solid and liquid phases occur) and electrostatic interaction.²¹⁷ Similarly, two mechanisms have been reported on the removal of methylene blue on base-treated wheat straw infused with Fe₃O₄ termed as ion exchange and surface composite. This surface composite is formed by the association developed between adsorbates and various functional groups present on the adsorbent surface and an electrostatic interface is developed between adsorbents and adsorbates.²¹⁸ Rhodamine dye showed adsorption on coffee powder as an adsorbent, and this process was supported by electrostatic intermolecular attraction between adsorbent and adsorbate molecules.²¹⁹ Cojocaru *et al.*, reported that the mechanism followed by acid orange dye removal on the adsorption surface is H-bonding.²²⁰ A similar mechanism for the removal of methylene blue on the prepared adsorbent surface was proposed by Siddiqui *et al.*²²¹ There are other mechanisms, including $\pi-\pi$ interactions or pi-effects, which resembles electrostatic



Adsorption mechanism

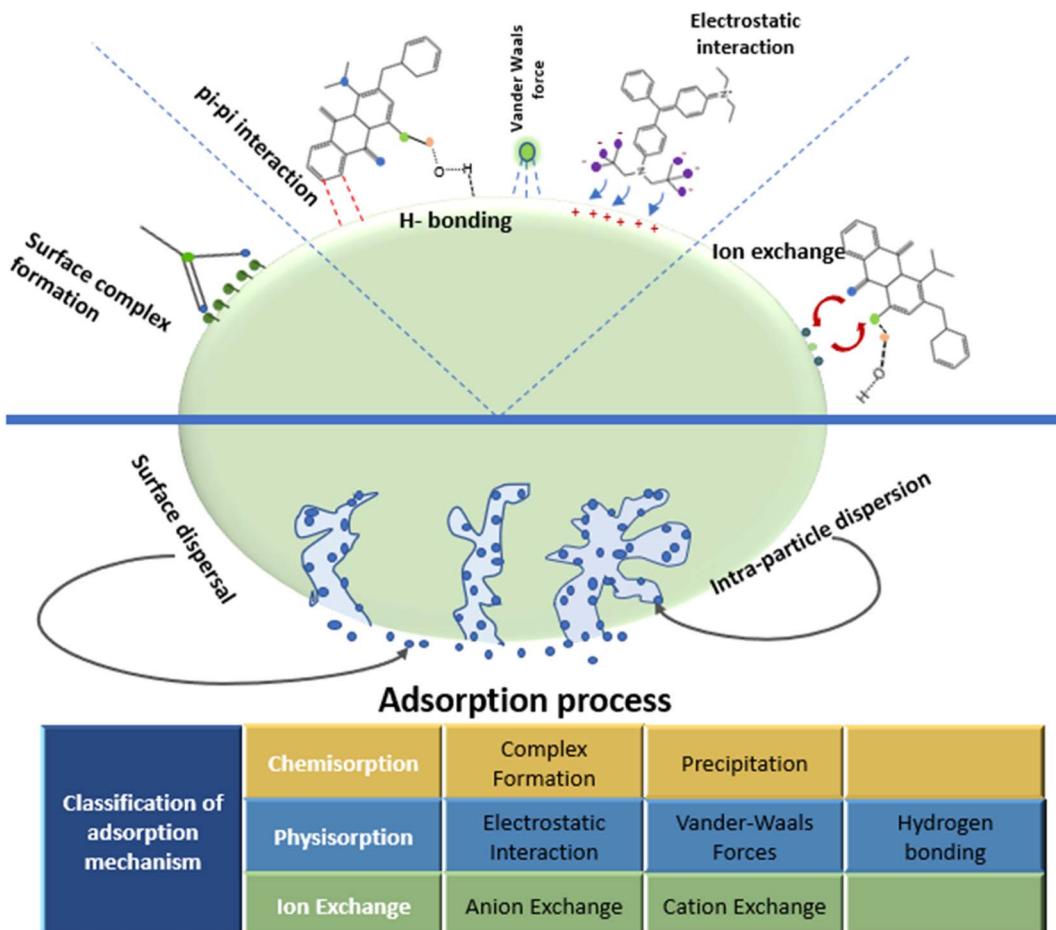


Fig. 6 Brief representation of the classification of adsorption mechanisms adopted by the dye removal process.²²³

Table 6 Previous studies on the desorption and regeneration of adsorbents

Adsorbent	Dye name	Dye class	% age recovery	References
Deoiled soy	Congo red	Anionic	90	229
Bottom ash	Congo red	Anionic	80	
<i>Corynebacterium glutamicum</i>	Reactive black 5	Anionic	80	230
Maize waste	Basic blue	Cationic	0	
	Acid blue	Anionic	12	231
	Reactive blue	Reactive	40	
Pine cone	Acid green 25	Anionic	26.95	79
	Acid black 26	Anionic	93.16	
	Acid blue	Anionic	98	

interaction, as positively charged entities interact with negatively charged entities. There are also some findings about the adoption of multiple types of mechanisms by the adsorption process, simultaneously. Thamer *et al.*, reported the adsorption of Coomassie brilliant green R 250 dye by three distinct mechanisms followed, namely, pi-effect, H-bonding, and electrostatic attraction.²²²

8. Desorption study

To propose the mechanism adopted by the adsorbate adsorbed and also to regenerate it, desorption studies are carried out. The rate of desorption directly related to the primary instigator and the kinetics of desorption help in finding the pattern of effluent transport.²²⁴⁻²²⁶



Eluents or solvents used for desorption play a significant role in the separation of adsorbents and adsorbates, and the selection of eluents depends on the adsorbate-adsorbent system.¹⁰ Various criteria are checked for the selection of eluents for the desorption process, which include compatibility with the adsorbate and adsorbent, easy breakage of interaction with the adsorbate from the adsorbent, pH, and complex formability.²²⁷ Various different solvents or eluents, such as 0.05 N HNO₃ (ref. 78), 2% HCl,⁹⁶ 0.1 M HCl²³ (acidic eluents), 0.1 M NaOH,⁸⁷ 0.15 M NaOH⁷⁵ (basic eluents), 4% NaOH + 2% NaCl,⁷ and 0.005 M thiourea in 1 M HCl⁵⁶ are commonly used by different scientists.

Desorption is carried out by adding some appropriate solvents (eluents) into dye-rich solutions and shaken till the dye gets extracted into that solvent by filtration and evaporated at elevated temperatures. Then, the spectrophotometric determination of dye is made.²²⁸ Similar studies carried by the scientists are presented in Table 6.

9. Conclusion

This study presents the recent work done by researchers on the adsorption of dyes using plant wastes, as there is a lot of work going on in this field and there is much scope for future work because of the leading issues we are facing, called water pollution. In this review, we have tried to simplify the evaluation of two classes of dyes, cationic and anionic, and their removal using agricultural by-products. Herein, it is concluded that the plant wastes coming out from agriculture industry can be utilized efficiently for the removal of dyes and cationic dyes, which showed more affinity towards natural forms of adsorbents than anionic dyes. A number of different modification techniques can be used to get their efficiency to be enhanced especially for the anionic type of dyes. The parameters responsible for better dye uptake by adsorbents include pH value (adsorption of cationic dyes favored at high pH values and anionic dyes prefer low pH values). Similarly, the adsorbent dose and dye concentration also affect the adsorption rate along with the temperature of the solution. The Langmuir and other isotherms were also examined to get the adsorption abilities of different adsorbents derived from agricultural wastes, and the results indicate that most of them showed more adsorption capacity towards cationic dyes than towards anionic ones. Moreover, kinetic studies presented here suggest the pseudo-second-order model to be followed more by both types of dyes. The adsorption characterization based on the morphology, surface area, and pore size using advance techniques present the adsorption ability of adsorbents. This review is mainly focused on plant source adsorbents along with their adsorption capacities. Hence, this review presented a comprehensive evaluation of plant wastes used in dye removal and their impacts on waste water treatment, which had shown great potential towards the green solutions to this problem.

Several studies consider adsorption as one of the most effect methods of dye removal from wastewater; however, there is always some room for improvement, so is here. These challenges are associated with the development of cost-effective,

highly efficient, and stable adsorbents. Hence, agricultural wastes, non-toxic industrial by-products, and biodegradable nanomaterials can be considered as alternatives.

Moreover, the term reusability is broader in its concept, which assures the maximum restoration and stability of spent adsorbents to get them reutilized effectively. Moreover, the disposal of the used adsorbents in the development of biochar or other energy-producing products is another economic aspect of the project.

Data availability

All data are presented here along with references.

Conflicts of interest

We have no conflict of interest regarding publication of this paper.

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