Review Article

PHYSICAL CHEMISTRY RESEARCH
Published by the
Iranian Chemical Society
www.physchemres.org
info@physchemres.org

Phys. Chem. Res., Vol. 12, No. 2, 361-382, June 2024
DOI: 10.22036/pcr.2023.396003.2332

Industrial By-Products as Potentially Economic and Promising Adsorbents for Removing Dyes from Effluents: A Review Study

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(Received 6 May 2023, Accepted 17 August 2023)

Exposure to pigments from waste effluents, which is visible through some amount of dyes in polluted water, has been referred to as a serious environmental threat and can have ruinous effects on both humans and the ecosystem. Lately, the development of technologies that can diminish contaminants to an acceptable level has received increased attention. Of all the developed techniques for eliminating contaminants from wastewater, biosorption is one of the most popular ones. Adsorption is an effective method to treat chromatic components in effluents and protect the ecosystem. Diverse categories of economic and productive adsorbents that are compatible with the ecosystem are utilized to remove dyes. Amongst the economic adsorbents, the utilization of industrial wastes is common due to their low cost, optimal yield, facile availability, excellent recyclability, and high adsorption capacity. Based on previous studies, FA, iron-containing waste, and blast furnace dust are the industrial by-products that have been reported to have a favorable percentage of removal efficiency (%) and the adsorption capacity to remove dyes under optimal conditions, which confirms their potential and unique characteristics for dye removal. This study aimed to examine various types of dyes and their detrimental effects as well as the process of biosorption. Additionally, the utilization of industrial by-products as promising adsorbents to eliminate dyes from wastewater and their potential implications for the industry are thoroughly discussed.

Keywords: Low-cost adsorbents, Pollutants, Water, Biosorption

INTRODUCTION

Chemical pollution of water is caused by an extensive range of poisonous derivatives, specifically industrial dyes. Industrial effluents are among the most significant origins of ambient contaminants, and the concentration of contaminated compounds in them often reaches tens of thousands of milligrams per liter [1-2].

Pigments of effluent generated by diverse industries, including textile, paper, plastic, and rubber industries, radioactive effluents, herbicides, petroleum hydrocarbons, dyes, cosmetics, chemical waste, and extraction of metals, if discharged to the environment before being treated, can create plenty of serious problems for the environment. For example, effluent discharge into the water can release toxic components into the ecosystem and eventually lead to bioaccumulation in the environment [3-4].

The concentration of dye in effluent mutates depending on the type of industry. The pigment in dye wastewater is generally chemically and photolytically stable [5]. Also, its self-assembled aromatic structure makes its biological composition subsist unchanged, which poses the threat of a pending natural disaster and is responsible for the dimness color and bad smell of water [6-7]. Synthetic dyes possess an aromatic molecular structure, which makes them more stable and their biodegradation more difficult. During the

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generation of products, the dyes may not be fully utilized. Small amounts of dyes are released into the environment and cause a vast accumulation of dyes in the form of industrial effluent [8-10]. Pigments may have both direct and indirect pernicious effects on humans in the shape of tumors, cancers, and allergies. They can also interfere with the growth at diverse trophic levels, including protozoa bacteria, algae, plants, and animals [11]. Furthermore, dyes can pollute all living organisms and natural ecosystems, including soil, rivers, and groundwater. As a result, the ability to self-treat wastewater and develop biological treatment systems contaminated with dyes is of great significance to the environment [12-13].

Purification techniques are commonly divided into three principal groups: physical, chemical, and biological [14-15]. Sometimes, ultrasonic and electromagnetic radiation techniques are categorized into discrete classes. Since the dye is so apparent in the dye waste, it must be treated [16-17]. Physical and chemical methods used to reduce dyes to an acceptable amount include some processes such as membrane filtration [18], coagulation/flocculation [19], electrochemical precipitation [20], adsorption [21-22], ion exchange [23], extraction [24], mineralization [25], sonolysis [26], electrolysis [27], chemical reduction [28], and advanced chemical oxidation [29]. Amongst these processes, biosorption enjoys more diversity and efficiency and has attracted the attention of researchers owing to the fact that it is economical, highly efficient, reusable, and recyclable with a high level of removal efficiency in a broad range of pH levels.

In addition, this technique has gained more attention due to the easy availability of bio-waste and that it can be used with novel biosorbents to remove pollutant substances [30-32]. Biosorption is an autonomous physicochemical and metabolic method based on diverse mechanisms, including adsorption [33-34]. The biosorption process is beneficial when the concentration of pollution in the wastewater is low. The use of bio-adsorbents to eliminate pollutants is preferable due to their comparatively better yield, lower price, and fewer ecosystem concerns [35-36]. Economic concerns and biosorption capability are the main factors in comparing adsorbents since the cost of biosorbents changes based on their efficiency and accessibility of adsorbents [37-38]. Owing to the presence of several vigorous surfaces on the biosorbents created by pigment molecules, saturation from biosorbents can be restored by moving the occupied molecules from their surface using different pH levels of the aqueous media [39-40]. In the meantime, since various industries produce a vast amount of waste solids as by-products, the feasibility of utilizing these waste solids as an economical and highly efficient biosorbent with high capacity to eliminate pollutants is considerably important to environmental concerns [41-42]. Figure 1 depicts the two primary classifications of industrial by-products, namely carbon and mineral. Also, Fig. 2 displays the five most

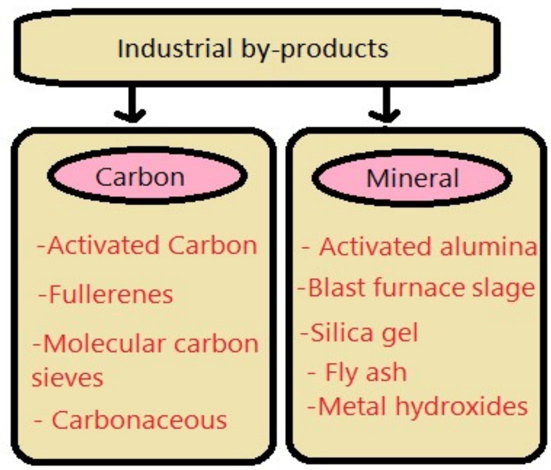

Fig. 1. Two main original classifications of industrial by-products.

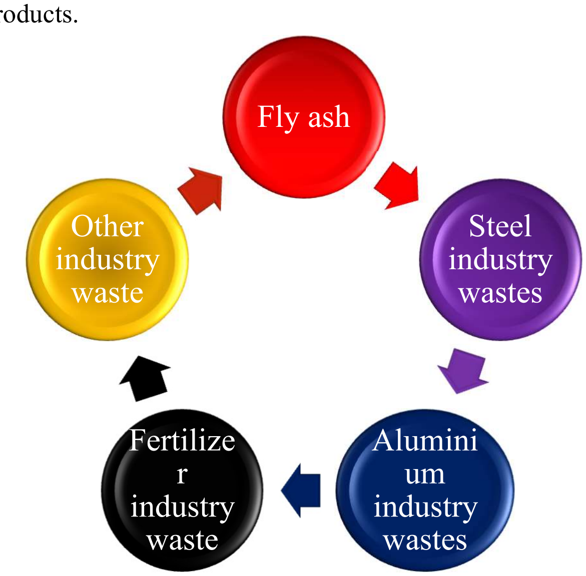

Fig. 2. Main classifications of industrial by-products as bio adsorbents.

widely utilized industrial by-products applied as biosorbents. The benefits of using these compounds are low cost, easy access, eco-friendly, no side-effects on waste disposal, appropriate recyclability, and excellent adsorption capacity [43-44].

The principal aim of this review study was to evaluate the potential use of industrial by-products as biosorbents, particularly the biosorption of toxic dyes. For this purpose, different types of dyes and the environmental hazards they impose as well as the biosorption process are discussed in detail. Also, the isotherms and kinetic and thermodynamic behaviors of the dye adsorption are concisely explained.

METHODOLOGY

In this study, a comprehensive review of approximately 170 articles directly relevant to color removal and surface absorption using biosorbents was conducted. The articles were sourced from reputable scientific databases, including Elsevier, Springer, and Wiley. Figure 3 presents the pattern of indexed papers concerning dye removal from wastewater. The data were retrieved from the Scopus database, and the figure illustrates a notable exponential growth over the past decade, indicating a rising interest in this subject within the scientific community.

Dyes

Dyes are compounds broadly employed in the textile, printing, rubber, cosmetics, plastics, and leather industries to dye products, a process that results in the generation of significant quantities of pigments from wastewater. Dyes are primarily categorized into anionic, cationic, and non-ionic pigments. Of all the dyes utilized in the industry, the textile industry ranked first in using dyes for dyeing fibers [1,45]. Dyes are chemical compounds that attach to tissues or surface shells. It is estimated that the textile and manufacturing industries use more than 10,000 commercial dyes worldwide. The consumption of dyes in the textile industry is more than 1000 tons per year, and about 10-15% of these dyes are disposed of during the dyeing process [46-47]. Then, they are released in water streams as effluents. Basically, the exact quantity of dyes released from diverse processes to the environment is unknown [48-50]. Main dyes have a high color severity and, even at low concentrations, are evidently visible in the wastewater. Multi-faceted pigments are largely founded on chromium, which is pathogenic [51].

Dyes may affect photosynthetic activity in aquatic animals by diminishing the permeation of light and may also be poisonous to some aquatic animals due to the presence of metals, aromatic substances, *etc*. In addition, they can cause intense human harm [52-53]. Dyes effluents, known as pigment effluents, are full of hazardous and poisonous chemicals, as shown in Fig. 4. Blue bodies containing

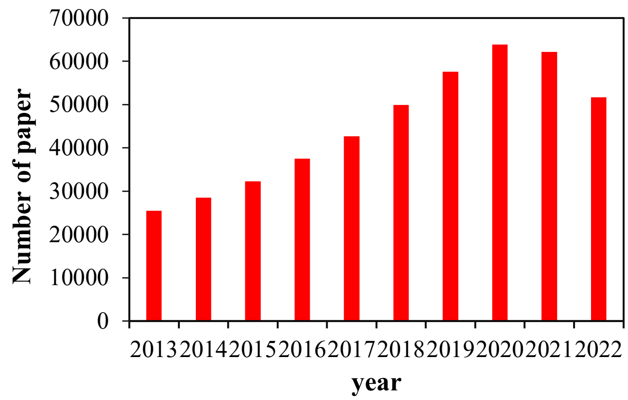

Fig. 3. The trend of indexed papers related to the subject published in the past decade. The data was collected from the Scopus database using the keywords "dyes" and "adsorption".

Fig. 4. Different Types of hazardous and toxic chemicals in dye effluents.

pigment effluents can be easily identified because their pigments cause turbidity and directly affect water transparency [54-55]. The presence of pigment in water sources is certainly not desirable because both humans and animals use water for their daily activities [56-57].

Today, eliminating pigments in aquatic resources has turned into a substantial ecological concern. There are various types of artificial dyes, which are tabulated in Table 1 based on their molecular structure [58-60]. However, dyes are sometimes categorized according to their solvability. Acid, basic, direct, mordant, and reactive dyes are solvable pigments while azo, disperse, sulfur, and vat are indissoluble pigments [61-62]. Amongst different types of pigments, azo dye, with 70% of generation, is the most widely used and frequently identified dye in the world. For this reason, artificial pigments must not be introduced into the ecosystem to combine with untreated aqua resources [63-64]. These noxious pigments have caused considerable anxiety among the public and environmentalists. Therefore, methods that can sequentially dispel one or more kinds of pigments from the body are highly welcomed [65-66].

Different Methods Used for the Disposal of Effluents

Water contamination originates from diverse sources, including households, industries, mines, and infiltration. However, one of the most significant sources of water contamination is the extensive release of wastewater by industries. Typically, water is classified into four categories: rainwater, domestic wastewater, agricultural water, and industrial wastewater [67-68]. In general, the challenges facing wastewater treatment are highly intricate due to the presence of diverse pollutants originating from different sources. Consequently, various types of effluents necessitate different specific treatment processes to deal with their specific characteristics [69-70]. Traditional approaches to metal removal face formidable challenges in meeting increasingly strict regulatory standards and their costs are on the rise. This has led to a growing demand for alternative and cost-effective technologies. Conventional methods for eliminating dissolved pollutants involve chemical precipitation, carbon adsorption, ion exchange, evaporation, and membrane processes [71-72]. Figure 5 depicts the common approaches employed to remove pollution from effluent.

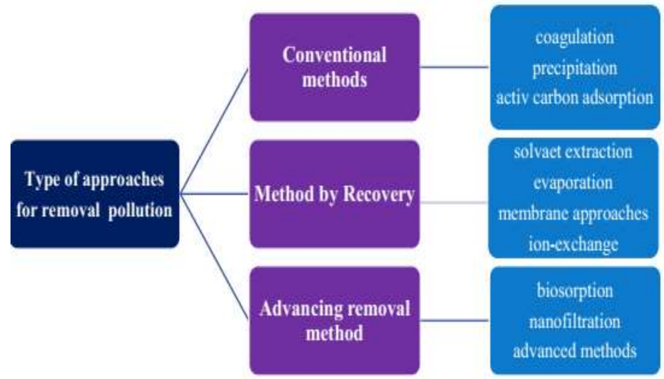

Fig. 5. Different types of approaches applied to the removal of pollution from effluent.

An Explanation of the Adsorption and Biosorption Mechanisms

Novel processes for the treatment of industrial effluents, including dyes, are usually utilized to diminish the toxicity of these contaminations against some treatment criteria. Lately, particular attention has been paid to novel methods for the physical and chemical removal of effluents; these methods include adsorption on new adsorbents, biomass sorption, membrane filtration, radiance, and electrochemical coagulation [73-74]. Today, some removal methods are available regarding customary dyes; these methods combine physical and chemical principles. One of the most significant methods based on physical removal is the adsorption method, which is an efficient method for eliminating contaminants such as dyes from effluents [75-76]. According to its energy, the biosorption procedure can be classified into two groups: physical adsorption and chemical adsorption (Fig. 6) [77-78].

Adsorption is an efficient, balanced, and cost-effective process for removing dyes from the effluent and treating water with high flexibility [79-80]. Its simple and uniform structure and heightened sensitivity to poisonous substances have made it a promising candidate for water treatment [81-82]. The idea of “biological adsorption” is multidimensional and has been developing over recent decades [83-84]. The uniqueness of the term “biological adsorption” can be linked to the fact that it reflects a multitude of mechanisms, use of biosorbents, consideration of ecosystem factors, and the presence or absence of metabolic activities in living organisms [85-86]. As a branch of biotechnology, biological

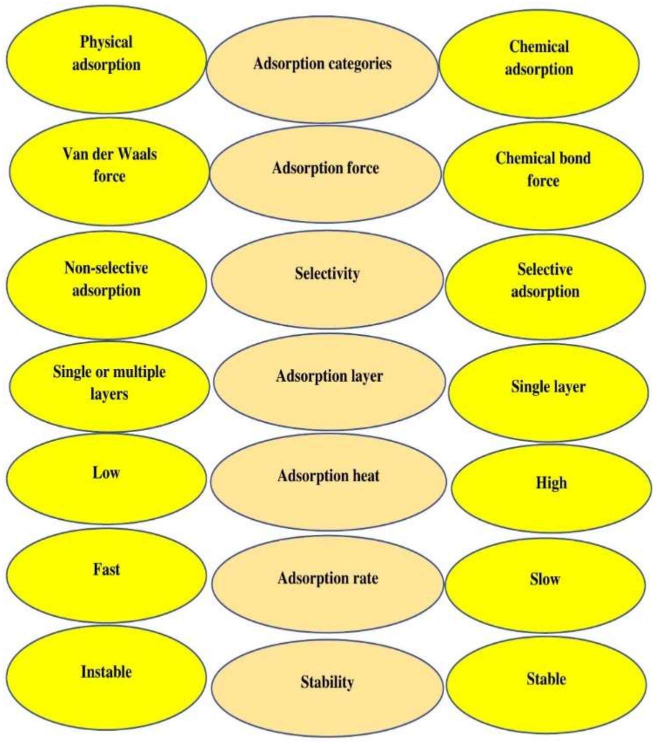

Fig. 6. A comparison of adsorption types.

adsorption is done using biological materials, which may contain living or non-living organisms and their ingredients, seaweed, or agricultural and innate wastes. Most recently, this method has been hailed as a hopeful and economic approach to biotechnology. Overall, biological adsorption is a physicochemical method that may simply be defined as eliminating materials from aqueous media using biotic factors [87-88]. Every type of biological substance has a great propensity to mineral and inorganic pollutants and has a unique potential for adsorption in myriad of biological substances. Biological substances are commonly used as biosorbents in the biosorption of a family of new materials based on renewable or waste biomass materials and usually do not require any specification before use [89-90]. The potential of bio-adsorbent materials renders them suitable for recycling wastewater streams and removing contaminants. Since the biosorption process is based on known adsorption principles, engineers are adequately familiar with the design and equipment used in it [91-92]. As the general understanding of this process and its fundamental mechanisms has enhanced, it is ready for to be applied more widely [93-94].

Type of Low-Cost Bio-Adsorbents

Every type of biological substance has a strong tendency for inorganic and organic contamination, meaning that there is a unique adsorption capacity in countless biological substances [95]. In the search for extremely efficient and economical biomaterials, new possibilities for the control of contamination, material recovery, and microbial, plant, animal, and industrially-derived biomass recycling have been explored [96-97]. Typically, economical adsorbents can be divided into five main classes, including (I) agricultural waste, (II) industrialized by-products, (III) sludge, (IV) marine, and (V) soil and minerals [98-99]. Amongst low-cost bio-adsorbents, the use of agricultural waste/by-products as bio-sorbents is of overriding significance in eliminating pollution from effluents [100].

Agricultural waste, particularly those with a great percentage of fiber, contains functional groups such as carbonyl, alcoholic, phenolic, and ether groups that have an extraordinary potential to bind metal ions or dyes [101-102]. Among the agricultural waste with the above-mentioned origin, the most popular ones utilized to remove dyes include coconut shell, orange peel, pomegranate peel, banana peel, pumpkin peel, tea waste, pistachio peel, rice paddy ash, coffee powder, pomelo peel, garlic peel, and bagasse peat [103-104]. Also, marine litter from food supplement technology is considered a natural, low-cost, harmless, and biodegradable source. These materials contain lignin, cellulose, and hemicelluloses, which all have adsorbent sites such as carbonyl, carboxyl, amine, and hydroxyl groups that are able to absorb pollutant ions through ionic interactions [105-106]. In addition, marine materials such as oysters, snails, and shrimp are not only easily accessible and abundant but also highly biodegradable and thus are among cheap biosorbents [107]. The shells of these materials are used as highly effective and economical biosorbents in eliminating contaminants due to their cavities, high roughness, and active sorption sites on their surface. The main constituent of these shells is ($CaCO_3$), which facilitates the control and reduction of pollution on the active sites of these biosorbents [108-109]. Soils also play a role in treating effluent found in contaminated groundwater or rivers. The most important process affecting pollutants in the soil is the adsorption of

Table 1. Various Types, Applications, and Principal of Dyes

Toxicity	Application	Attributes	Samples	Dyes
Carcinogenic (benign and malignant tumors)	Nylon-wool-silk-paper-leather-inkjet printing	Water-soluble	Acid Red 183-Acid Orange 10 and 12-Acid Orange 8-Acid Red 73-Acid Red 18-Yellow-Orange-Acid Green 27-Methyl Orange-Amido Black 10B-Indigo Carmine	Acidic
Carcinogenic (benign and malignant tumors)	Paper-polyacrylonitrile-corrected nylons-used in medicine as disinfectant.	Soluble in water-releases colored Cations in water. Some of these strains show physical activity	Methylene blue-green Janus-green game 5-purple game 10-rhodamine 6	Cationic
Allergic-carcinogenic	Polyester-nylon-cellulose-cellulose acetate-acrylic fibers	Insoluble in water -non-ionic- for the hydrophobic aqueous part	Scattering orange 3-Scattering red-Scattering red 1-Scattering yellow 1	Broad cast
Bladder cancer	Yarn-regenerated cellulose-paper-leather	Water-soluble, anionic, wash speed and council improve the formation of chelates with metal salts	Congo Red - Straight Red 23 - Straight Orange 39 - Straight Blue 86	Direct
Dermatitis-Conjunctival swelling-Ocular allergy-Occupational asthma	Yarn-wool-nylon-textile inkjet printing-	Very high wash speed due to covalent bond formation with fibers-lighter than direct dyes	Black and Activator 5-Green Reactor 19-Blue Reactor-Red Reactor 195-Blue Reactor 19-Red Reactor 120	Reactive
	Cellulose fibers	After reducing them in an alkaline bath (NAOH)-use colorless soluble salts	Blue-blue 4-Green green 11-Orange yellow 28-Yellow yellow 20	Vat

metals from the liquid phase to the solid phase [110-111]. There have been many studies on soil adsorption behavior, but these studies have focused on only a few types of soil. The most common types of soil investigated for the removal of contaminants include clay, red mud, and zeolite. Clay adsorption potency is related to the negative load of granulated silica inorganic composition. This charge is neutralized by the adsorption of the positive load of cations such as dyes. Clay can be altered to increase its yield by eliminating contaminants from water and wastewater [112]. Rose is a waste product that is molded in the generation of Al_2O_3 when the $Al_2H_2O_4$ ore is subjected to leaching. This usually includes about two tons of mud per one ton of factory-built alumina. In short, roses are a good adsorbent for removing pollutants, including dyes [113].

Layered silicate clay minerals play a vital role in soil and are crucial for adsorbing pollutants. These minerals consist mostly of planes of oxygen atoms, with silicon and aluminum atoms forming ionic bonds to hold the oxygen atoms together. Each layer typically comprises three or four planes of oxygen atoms with silicon and aluminum ions in between [114]. The negative charge of these clay minerals arises from the replacement of silica (Si^{4+}) with aluminum (Al^{3+}) in their mineral structures. This process, known as amorphous substitution, leads to clays with a negatively charged surface.

Cation adsorption occurs due to the negative charge on the clay mineral layers. The primary mechanism governing this process, as evidenced by activation energies of the reactions, is called ion exchange or cation exchange between the adsorbent and dye ions [115-116]. Naturally occurring or commercially produced Zeolites are also silicate minerals. Sand, sediment, soil, and minerals are used to destroy organic pollutants in water [117]. In addition, other classes of microorganisms consist of bacteria, algae, and fungi. Nevertheless, fungi are utilized to eliminate dyes owing to the presence of chitin in their cell walls. They are able to put pigments in their cell structure and eliminate them at the connectivity [118]. As the earliest species of agronomical, algae are a significant class of living organisms that are home to nearly 40,000 kinds of organisms. Algae are generally grouped into two classes, eukaryotes and prokaryotes, which have reflexive groups such as NH_2, -OH, -COOH, SO_4, *etc.*, in their structures. The creation of chemical bonding with dye molecules is considered to be the basic parameter in the biological adsorption potential of algae [119-120]. Bacteria are also a major group of single-celled organisms in soil and water. They are ubiquitous, making up an important portion of the total terrestrial biomass of about 1018 grams. Bacteria are more involved in the biological uptake of metal than other organisms owing to the presence of different functional groups in their cell walls. These substances contain specific functional groups, and the removal of dyes by living and dead biosorbents by bacteria has been extensively investigated by researchers [121-122]. Most single-celled organisms, which belong to prokaryotes found in soil and water, coexist with other organisms in various forms. Different shapes of bacteria include spherical (*e.g.*, Streptococcus), rods (*e.g.*, Bacillus), spirals (*e.g.*, Rhodospirillum), and filaments (*e.g.*, Sphaerotilus natans). This variation and the nature of various functional groups of bacteria have given them a very favorable sorption capability to remove pollutants [123-124]. Also, industrial waste has received much attention due to its unique potential in eliminating pollutants, in general, and dyes, in particular.

Industrial By-Products

The most common industrial wastes used as adsorbents to remove pollutants are fly ash (FA), steel waste, aluminum waste, sullage, and paper production effluent. FA is a residue substance produced during ignition processes [125-126]. Reuse and recovery are the main approaches to dealing with rigid effluents. In fact, FA, an industrial waste, is a compound produced during charcoal burning with suspended particles and is being produced at a fast rate in the industry due to the high demand for electrical appliances, leading to the annual discharge of billions of tons of FA around the world [127-128].

FA has a large, irregularly porous structure with an excellent surface and good biosorption capacity. The FA specification primarily depends on the kind of charcoal and burning circumstances. Moreover, FA includes important oxide ingredients, such as silicon dioxide, aluminum oxide, calcium oxide, magnesium oxide, sodium oxide, titanium dioxide, and basic elements, including phosphorus, potassium, magnesium, zinc, iron, and manganese. Therefore, FA has been studied by many researchers. Wind ash is a mixture of powdered coal combustion at high temperatures, and, with a chemical structure similar to argil, has an excellent ability to bind to limestone. Thus, FA can be used as a low-cost adsorbent to remove contaminants due to its unique properties, such as specific surface area, porosity, and particle size [129-131]. Steel slag (SS) is a liquid effluent formed during steel production, with about 150 kg of SS generated for each ton of steel produced. Landfilling is the most common technique for disposing of SS; nonetheless, it affects a huge quantity of agronomic land. Moreover, unintended and unreliable waste disposal approaches pose many serious dangers to the ecosystem [132-133]. Currently, the use of SS in only China is around 30%, a relatively high percentage which highlights the importance of developing methods to reuse SS. SS is suitable for wastewater treatment due to its properties such as great mechanical stability, strong acid and alkali resistance, favorable thermal properties, and unique chemical structure. Moreover, what makes SS a promising candidate for treating wastewater is its high availability and low cost. SS is basically composed of CaO, SiO_2, P_2O_5, FeO, Fe_2O_3, MgO, MnO, and Al_2O_3. In recent years, researchers have increasingly considered the use of SS in wastewater treatment [134-135].

The slag generated is divided into two main categories: kiln slag and steel-making slag. Kiln slag is produced during the process of extracting iron from iron ore, coke, and fluxes through smelting operations. On the other hand, Steel-making Slag is formed during the refining process when fluxes react with nonferrous oxides and unwanted elements in the raw materials while in a molten state, converting crude iron into steel. The main difference between kiln slag and SS is the concentration of iron in them. FeO level in kiln slag is roughly 0.70%, but the total iron content in SS ranges from 16% to 25%. It has also been documented that the chemical composition of slag affects the properties of concrete [136-137]. Aluminum scrap is a by-product of the aluminum smelting industry and is composed of metal, salt oxides, and other non-metallic materials. Worldwide, five million tons of aluminum waste is generated annually, and it has been used to produce cans, tins, aluminum siding, and other related aluminum products. One of the useful applications of the above-mentioned materials is in wastewater and water treatment [138-139]. The waste slurry produced during fuel combustion in herbage has been utilized as a low-carbon adsorbent. According to previous studies, the waste slurry is primarily washed with H_2O_2 and burned at 200 °C to stop the formation of grime following the next steps of treatment, producing a favorable material with a specific surface of 1630 m^2 g^{-1} [140]. This product has a high potential to remove contaminants. Other industrial wastes that effectively remove pollutants include waste from the sugar industry. Bagasse has also been utilized as an adsorbent to remove various contaminants from water. Finally, steel mills produce large volumes of granulated blast furnace slag as a by-product, but it has been used as a low-cost adsorbent for eliminating poisonous organic contaminates from water and wastewater [141-142].

Mechanism of Adsorption

The probable adsorption mechanisms of dye molecules to biosorbents include physical and chemical adsorption, electrostatic reactions, H_2 bond, π-π reactions, and precipitation. The possible mechanism responsible for the biosorption of dyes to a biosorbent is shown in Fig. 7. This figure highlights the fact that biowaste has different negative load functional groups on its surface, including NHR_2, C=O, -COOH, and-OH groups. In addition, dye molecules may be adsorbed on the holes and hollows on the surface of biosorbents. It can be stated that electrostatic reactions among positive and negative color molecules of biosorbents enhance the adsorption capacity [143-144].

In addition, other forces, such as van der Waals, hydrogen bonding, and hydrophobicity, might be responsible for the biosorption of molecular dyes on the surface of adsorbents produced as biowaste. Figure 7 demonstrates the mechanism

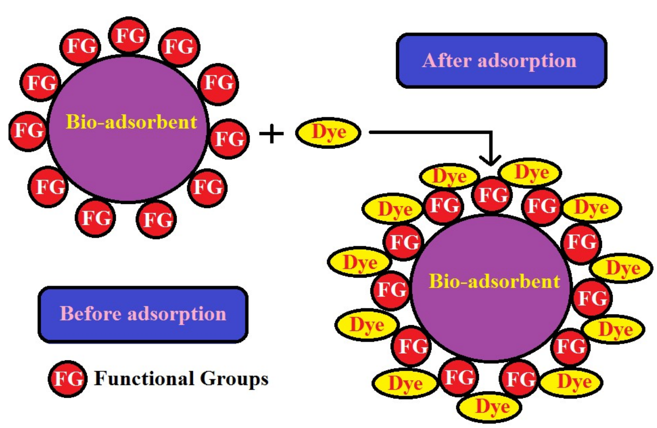

Fig. 7. A possible mechanism responsible for dye adsorption.

of dye adsorption. Physical adsorption also occurs when weak gravitational forces, such as van der Waals forces, are present in the reaction between the adsorber and the dye molecules. Van der Waals forces are electrostatic interactions resulting from temporary fluctuations in a dipole moment within atoms or molecules, causing neighboring atoms or molecules to undergo a similar shift. These forces are non-specific and can occur between molecules with any chemical structure. Although individual van der Waals bonds are short-lived, they can collectively form more stable links between the adsorbent and its surface, preventing desorption. When adsorbate molecules are held on the surface of an adsorbent through Van der Waals forces or weak physical interactions, it is known as physical adsorption, Van der Waals adsorption, or physisorption [145-146]. Chemical adsorption also happens when robust chemical gravitational forces are present in chemical bonds [143-144,147].

Discussion of Industrial By-Products as Low-Cost Adsorbents

Several studies have been conducted on the removal of dyes by industrial wastes. Table 2 summarizes the optimal conditions for the processes of adsorption by industrial wastes. Adsorbents derived from industrial wastes consist of valuable oxide components, such as silicon dioxide, Aluminum oxide, calcium oxide, magnesium oxide, sodium oxide, titanium dioxide, and essential elements, including phosphorus, potassium, magnesium, zinc, iron, and manganese. Consequently, industrial wastes have garnered significant attention from researchers, and their potential utilization as affordable adsorbents for contaminant removal has been emphasized. This is due to their distinctive

Table 2. Optimal Conditions of Different Industrial By-products in Removing Dyes from Water and Wastewater

Bio-adsorbent	Dyes	pH	Conc. (mg l^{-1})	Dose (g l^{-1})	Temp (°C)	Time (h)	Removal efficiency (%)	q_{max} (mg g^{-1})	Ref.
Aluminum foil waste	Reactive green-19	3	100	0.025	25	1.5	98.65	133.33	[149]
Iron-containing waste	Methyl orange	2	20	0.2	25	0.5	99	-	[150]
Fly ash	Methylene blue	10	-	-	40	70-80	-	0.014 mmol g^{-1}	[151]
Blast furnace sludge	Bismark Brown R	5.5-6.5	0.046	0.01	25	0.41	-	85	[152]
Blast furnace sludge	Rhodamine B	5.5-6.5	0.047	0.01	25	0.41	-	91.1	[152]
Fertilizer plant waste carbon	Auramine-O	7	20	1	25	4	-	246.9	[153]
Fertilizer plant waste carbon	Congo red	7	20	1	25	4	-	233.86	[153]
Fertilizer plant waste carbon	Orange-G	7	20	1	25	4	-	236.07	[153]
Fertilizer plant waste carbon	Methyl violet	7	20	1	25	4	-	240.26	[153]
Carbon slurry waste	Congo red	5.5-6.5	200	1	25	2	95	272	[154]
Fly ash	Methylene blue	10	-	0.1	30	24	-	590	[155]
Blast furnace dust	Ethyl orange	7	0.163	1	25	0.75	-	198.4	[156]
Blast furnace dust	Metanil yellow	7	0.187	1	25	0.75	-	211.9	[156]
Blast furnace dust	Acid blue 113	7	0.34	1	25	0.75	-	221.2	[156]
Fly ash	Crystal violet	8	203	5	25	40	About 100	-	[157]

properties, including specific surface area, porosity, and particle size [148]. Based on previous results, the industrial by-products FA, iron-containing waste, and blast furnace dust have been found to have favorable removal efficiency percentage (%) and adsorption capacity to remove dyes under optimal conditions, confirming their potential and unique characteristics for removing dyes. Ghulam *et al.* utilized aluminum foil waste to synthesize alumina to remove reactive green-19 dye [149]. They reported an adsorption efficiency of 98.65% in optimal conditions, which included a pH of 3 for 90 min with adsorbent doses of 0.025 g l^{-1} and 100 mg l^{-1} of dyes at 25 °C. In addition, the highest adsorption capacity of 133.33 mg/g was achieved from the Langmuir equation. In another study, Ali *et al.* used iron-containing waste to remove methyl orange dye, which was found to have an adsorbent dose of 0.2 g l^{-1} at 20 mg l^{-1} of orange dye at 25 °C for 30 min [150]. The optimal adsorption efficiency reached 99%. Wang et al. studied the removal of methylene blue dye by FA at the optimal conditions of pH = 10 and a duration of 70-80 h at 40 °C [151]. They reported an adsorption capacity of 0.014 mmol g^{-1}. Bhatnagar *et al*. used blast furnace sludge as an adsorbent to remove rhodamine B and Bismark Brown R dyes [152]. They reported that 0.046 mg l^{-1} of Bismark Brown R and l0.047 mg l^{-1} of rhodamine B reached the maximum adsorption capacity to remove 85 and 91.1 mg g^{-1} of cationic dyes, respectively. Mall et al. examined the application of fertilizer plant waste carbon to remove Auramine-O (AR), Congo red (CR), Orange-G (OG), and methyl violet (MV) dyes [153]. They applied 1 g l^{-1} of the adsorbent with a concentration of 20 mg l^{-1} for 4 h at 25 °C and achieved 246.29, 233.86, 236.07, and 240.26 mg g^{-1} dye removal for AR, CR, OG, and MV, respectively. Bhattacharyya and Sharma used carbon slurry waste obtained from National Fertilizer Limited to remove Congo red dye at an optimal condition of pH = 5.5-6.5 for two hours at 25 °C with 200 mg l^{-1} of Congo red dye and a biosorbent dose of 1 g [154]. The maximum adsorption capacity and efficiency reached were 272 mg g^{-1} and 95%, respectively. Wang *et al.* found that methylene blue dye could be removed using FA, which reached an adsorption capacity of 590 mg g^{-1} in 24 h at a pH of 10, an adsorbent dose of 0.1 g l^{-1}, and a temperature of 30 °C [155].

Jain *et al.* used blast furnace dust to remove ethyl orange, methanol yellow, and acid blue and reported that they reached 198.4, 211.9, and 221.2 mg g^{-1} dye removal for 0.163, 0.187, and 0.34 mg l^{-1} of ethyl orange, methanol yellow, and hydrochloric acid, respectively, under the optimal condition with a pH of 7, for 45 min, at 25 °C, and an adsorbent dose of 1 g l^{-1} [156].

Mohan *et al.* used FA to remove the crystalline purple dye under the optimal condition, which consisted of a pH of 8 for 40 h at 25 °C, a concentration of 203 mg l^{-1}, and a biosorbent dose of 5 g l^{-1}, and obtained almost 100% removal efficiency [157].

Isotherm, Kinetic, and Thermodynamic Studies

Isotherm patterns are generally investigated to describe the mechanism governing the adsorption technique and its structure and are used to estimate maximum color adsorption. The isotherm shows the parallel between the adsorbed ions on the biosorbent and the aqueous media at a specific temperature. Square R (R^2) is each significant factor selected for the sorption isotherms used. If R^2 is closer to 1, the experimental data obtained will be more consistent with the model under study. Common Freundlich and Langmuir isotherm models primarily regulate the adsorbent performance [158-159].

Kinetic models are particularly important for studying adsorption processes to eliminate toxic dyes. The interaction and adsorption rates are analyzed in the adsorption methods using adsorption kinetics. The most commonly used kinetic models are pseudo-first-order (QFO) and pseudo-second-order (QSO) kinetic models [160-161]. In the QFO model, while physisorption is assumed to limit the adsorption rate of the particles onto the adsorbent, chemisorption is assumed to act as the rate-limiting mechanism in the process. Sten Lagergren (1876-1922) introduced the pseudo-first-order model, which can be represented by the following linear equation:

$$dq_t/dt = k_1 (q_e - q_t) \tag{1}$$

where q_e and q_t (mg g^{-1}) are the quantities of dye adsorbed at equilibrium and at a specific time (t) in minutes, respectively. The rate constant k_1 (1/min) corresponds to the first-order rate constant. By applying boundary conditions in Eq. (1), where $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (1) results in Eq. (2):

$$\log(q_e - q_t) = \log q_e - k_1 t \quad (2)$$

When employing the QFO kinetic model, plotting $\ln(q_e - q_t)$ against time (t) results in a linear relationship. The slope and intercept of this line can then be utilized to determine the rate constant (k_1) and the quantities of dye adsorbed at equilibrium (q_e) [162-163]. Another commonly used adsorption model known as the QSO model is presented in Eq. (3) below:

$$dq_t/dt = k_2(q_e - q_t)_2 \quad (3)$$

The velocity constants for the two kinetic models are represented by K_1 (1 min^{-1}) and K_2 (g mg^{-1} min^{-1}), respectively. Additionally, q_e (mg g^{-1}) denotes the adsorbed amount at equilibrium for both models while qt (mg g^{-1}) is the adsorbed amount at any given time (t) in minutes, reflecting the contact time [164-165]. Table 3 summarizes the isothermal and kinetic models used in applying industrial wastes to remove dyes. It is clear from Table 3 that most studies have followed the Langmuir and Freundlich isotherm models and the QFO kinetic model.

In thermodynamic studies, the thermodynamic factors ΔS°, ΔH°, and ΔG° have been computed using Eqs. (4)-(6).

$$\ln K_{eq} = C_{ads}/C_e \quad (4)$$

$$\ln K = \Delta S°/R - \Delta H°/RT \quad (5)$$

$$\Delta G° = \Delta H° - T\Delta S° \quad (6)$$

where K_{eq} is the equilibrium constant, C_{ads} is the amount of dye adsorbed (mg g^{-1}), C_e is the concentration of dyes in equilibrium aqueous media (mg l^{-1}), R is the gas constant (814.3 mol kg^{-1}), and T is the temperature of the absolute aqueous media. Slopes and latitudes from the original plot are used to calculate ΔH° and ΔS°. Negative ΔH°, ΔS°, and ΔG° values demonstrate that the biosorption technique is exothermic [166-167].

The entropy is reduced at the solid-liquid phase transition, and the biosorption processes happen spontaneously. Entropy is a measure of disorder that significantly affects various aspects of our daily lives. When left uncontrolled, disorder increases over time, leading to the dispersion of energy and the transformation of systems into chaos. The experimental calculation of adsorption entropy involves measuring heat capacity and observing adsorption behavior in equilibrium experiments and temperature-programmed desorption, in which it is assumed that the rates of adsorption and desorption are equal.

Table 3. Isothermal and Kinetic Models Used in Various Industrial By-products for the Removal of Dyes

Bioadsorbent	Dyes	Fitted Isotherm model	Fitted Kinetics model	Ref.
Aluminum foil waste	Reactive green-19	Langmuir	-	[149]
Iron-containing waste	Methyl orange	-	QFO	[150]
Fly ash	Methylene blue	Redlich-Peterson	-	[151]
Blast furnace sludge	Bismark Brown R	Langmuir	QFO	[152]
Blast furnace sludge	Rhodamine B	Langmuir	QFO	[152]
Fertilizer plant waste carbon	Auramine-O	Freundlich	QSO	[153]
Fertilizer plant waste carbon	Congo red	Freundlich	QSO	[153]
Fertilizer plant waste carbon	Orange-G	Freundlich	QSO	[153]
Fertilizer plant waste carbon	Methyl violet	Freundlich	QSO	[153]
Carbon slurry waste	Congo red	Langmuir	QFO	[153]
Blast furnace sludge	Ethyl orange	Langmuir	QFO	[156]
Blast furnace sludge	Metanil yellow	Langmuir	QFO	[156]
Blast furnace sludge	Acid blue 113	Langmuir	QFO	[156]
Fly ash	Crystal violet	Freundlich	QFO	[157]

Regarding entropy, ΔS represents the changes in the level of order or disorder in the reaction. An increase in order results in a negative ΔS value while a decrease in order yields a positive ΔS value. Generally, the change in entropy (ΔS) during an adsorption process is negative [168-169]. Also, ΔG° values, which are $-20 < \Delta G° < 0$ kJ mol^{-1} for physical reactions and $400 < \Delta G° < -80$ kJ mol^{-1} for chemical reactions [170-171], generally indicate the type of isotherm. Table 4 summarizes the studies conducted on thermodynamic parameters with regard to industrial wastes for dye removal. It is clear from Table 4 that the processes performed were spontaneous and with increasing irregularity.

CONCLUSIONS

Numerous studies concerning the adsorption characteristics of various adsorbents for dye removal from wastewater have been published and discussed in this article. This review study emphasizes that using economic adsorbents in the adsorption process is highly cost-effective compared to conventional adsorbents. Among low-cost adsorbents, the use of industrial wastes as biosorbents to eliminate dyes from the environment is of particular importance. The advantages of using these compounds include low cost, high efficiency and capacity, easy maintenance and access, no waste disposal, proper recyclability, and ecosystem compatibility. In general, it can be said that the use of industrial wastes to remove dyes results in higher efficiency and adsorption capacity compared to other conventional adsorbents, which are much more expensive. A review of isothermal, kinetic, and thermodynamic studies on the adsorption method revealed that industrial wastes frequently followed Langmuir and Freundlich isotherm models and the QFO kinetic model. In addition, the values obtained from thermodynamic factors illustrated that the adsorption method is generally spontaneous and exothermic, and is accompanied by increased irregularities.

One of the limitations of this study lies in its focus on a limited number of industrial by-products used for dye removal in laboratory-scale experiments. However, this study highlights the fact that industrial by-products have the potential to be used as part of an innovative approach to promoting a pollution-free environment by treating industrial

Table 4. Thermodynamic Parameters Used in Various Industrial By-products for the Removal of Dyes

Industrial by-products	Dyes		ΔG° (kJ mol^{-1})		ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	Ref.
Fly ash	Methylene blue	- -	-38.6 (303°K)	-37.4 (313°K)	76.1	370.2	[151]
Blast furnace sludge	Bismark brown R	-26.5 (298°K)	-28.2 (313°K)	-	-0.81	86.2	[152]
Blast furnace sludge	Rhodamine B	-27 (298°K)	-29.7 (313°K)	-	-1.12	89.9	[152]
Carbon slurry waste	Congo red	-28.3 (298°K)	-28.9 (313°K)	-	-19.9	28.5	[154]
Blast furnace sludge	Ethyl orange	-28.3 (298°K)	-29.8 (313°K)	-	-6.2	74.2	[156]
Blast furnace sludge	Metanil yellow	-27.4 (298°K)	-28.9 (313°K)	-	-6.1	71.5	[156]
Blast furnace sludge	Acid blue 113	-26.5 (298°K)	-27.9 (313°K)	-	-5.8	69.5	[156]
Fly ash	Crystal violet	25.96 (283°K)	31.18 (298°K)	32.71 (313°K)	36.51	209.64	[157]

dye. Therefore, future research needs to concentrate on the development and utilization of industrial waste adsorbents in treating all types of effluents.

Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Abbreviation:

FA: Fly ash
SS: Steel slag
QFO: pseudo-first-order
QSO: pseudo-second-order
AR: Auramine-O
CR: Congo red
OG: Orange-G
MV: Methyl violet

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