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Biosorption of Azo Dyes by Bacterial Biomass: A review

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ABSTRACT

This review explores the potential of bacterial biomass as a sustainable and cost-effective approach for removing azo dyes from wastewater. Azo dyes, widely used in various industries, pose significant environmental challenges due to their persistence and potential toxic effects. The study provides an extensive analysis of the current literature on the biosorption of dye using bacterial biomass. It discusses the mechanisms involved in biosorption, including physicochemical interactions, microbial metabolism, and cell surface characteristics. The review presents an overview of different bacterial species, their suitability for biosorption, and the factors that influence their efficiency. The review critically evaluates various parameters affecting biosorption performance, such as pH, temperature, initial dye concentration, and biomass dosage. It highlights the importance of optimizing these parameters to enhance biosorption efficacy and maximize dye removal efficiency. The advantages and limitations of using bacterial biomass for azo dye biosorption and comparing it with other conventional treatment methods were discussed. The potential application of biosorption in large-scale scenarios and the challenges associated with its implementation are also addressed. The review emphasizes the need for further studies to explore novel bacterial strains, improve biosorption kinetics, optimize process parameters, and investigate the fate of dye-loaded biomass.

INTRODUCTION

Azo dyes have been the most commonly used synthetic dyes in many industries, including textile, cosmetics, food, and papermaking [1,2]. Environmental pollution resulting from the release of azo dyes from the effluents of such industries has been a serious issue around the world [3,4]. Effluents from azo dye utilizing industries are usually released directly into the water bodies and have been a significant wastewater treatment concern. Many of these azo dyes and their metabolites have been documented to be mutagenic and carcinogenic, as well as xenobiotics and recalcitrant pollutants [3,5,6]. Therefore, azo dyes have been reported to be dangerous to human health, the aquatic ecosystem, and the environment, even in small amounts. Other challenges of azo dye pollution include increasing the biological oxygen demand and chemical oxygen demand (BOD and COD), compromising the photosynthesis and the aesthetic quality of the waterbodies [7,8].

Due to the high solubility of these dyes in water, some of the conventional wastewater treatment processes do not effectively clean the contaminants [9]. Traditionally, to effectively treat azo dye effluents involves combining biological, chemical, and physical processes such as; precipitation, coagulation, flocculation, ion exchange, reverse osmosis, membrane filtration, photoelectrochemistry, incineration, etc. [10].

Nevertheless, because of excessive usage of chemicals in some cases, the implementation of this process may significantly generate secondary metabolites or sludge [11,12]. Furthermore, these conventional methods have also shown to have some disadvantages: high production and maintenance costs, low dye removal efficiency, and possible generation of toxic byproducts. In the alternative, biosorption has been researched and proclaimed as a promising technology in providing a safe, natural, economical, and comprehensive cleanup choice to remove several environmental contaminants [13,14].

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Biosorption is defined as a physicochemical process for removing a substance (organic or inorganic) from a solution using a biological material or its components (death or living) [15,16]. Biosorption mechanisms include adsorption, absorption, surface complexation, precipitation, and ion exchange. Biosorption has been seen to have a simple design, high performance, ease of operation, and low cost. Biosorption materials are widely available (e.g., agricultural and industrial wastes), and the process is swift, takes place between few minutes to hours [17]. Many biosorption studies were conducted with biomass of animals, plants, microorganisms (fungi, bacteria, and algae), and other byproducts on metals, dyes, and substances alike. Despite several studies on biosorption, there is still a gap in exploring its application on an industrial scale. This study is aimed to review the biosorption of azo dyes using bacterial biomass, efficacy, advantages, disadvantages, and prospects.

Azo dyes

Azo dyes are the most popularly known synthetic dyes that have been used extensively as colorants in many industries, including textile, photography/printing, food, pharmaceuticals etc., [1,18]. Generally, dyes are classified based on their solubility; soluble dyes include basic, metal complex, mordant, reactive, and direct dyes, while insoluble dyes include vat and azoic disperse, and sulfur dyes [19,20]. The Azo dye structure has one or two bonds (-N=N-) as part of its molecule responsible for its color (chromophore), **Fig. 1**. Besides, it has one or more aromatic structures. Azo dyes have high resistance against an oxidizing agent and higher photolytic stability. Common examples of azo dyes are Trypan Blue, Methylene Blue, Congo Red, Acid red, Basic Red, Brown HT, Brilliant Black, Alizarin Yellow, Azo Violet, Direct Blue, etc. [3,21].

The dye group, Azo, is the most adaptable and biggest class of dyes [1,22]. Its production is simple, cost-effective, available in different colors, easy to use, and durable [1,20,23]. Approximately, there are about 40,000 other colorants and dyes used across industries, and Azo dye production has been estimated to account for more than half (50%) of total annual dye production. Roughly 10 to 15% of dye used in the dying process are discharged into the environment as effluents and mainly to the water bodies [24,25]. Among all the dye-using industries, textile dying generates the most significant portion of the dying effluents, which was reported to have an average of 300 mg/L dye in the effluent [26]. Some of these azo dyes have also been known to contain surfactants, salts, and chlorinated compounds that make them more toxic [11].

Under natural environments, most Azo dyes are microbial resistant, non-degradable, difficult to remediate from wastewater using many methods [27,28]. Examples of azo dyes groups used in dying include polycyclic, triphenylmethane, and anthraquinone. They are categorized as recalcitrant, xenobiotics, mutagenic and carcinogenic [29]. They pose significant threats to the environment, including living aquatic organisms and animals. Some of the Azo dyes are highly, and non-highly hazardous, and exposure to these dyes could cause eye irritation, diarrhea, respiratory challenges, vomiting, cyanosis, nausea, profuse sweating, mental confusion, methemoglobinemia, jaundice, dyspnea, convulsions, and tachycardia. Therefore, the dyes demand extensive treatment before being discharged.

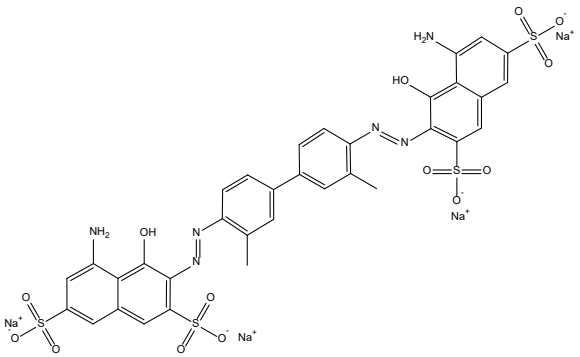

Fig. 1. Structure of an azo dye (Trypan Blue).

Toxicity and impact of dye pollution in the environment

Azo dyes have been extensively used in biomedicine staining, food, plastics, painting, and the textile industry for dying. These industries have produced a significant amount of solid waste, dirt slurry, and effluents. More so, traces of heavy metals are present in the dying effluents, such as lead, zinc, copper, and chromium [21,22]. The effluents are mostly passed into the water bodies through irrigation canals, waterways, farm fields [30]. When it gets into the environment, these effluents compromise their physical, chemical, and biological nature, such as pH, temperature, odour, turbidity, etc. [1,23]. In turn, this has significant health risks on the being of the aquatic, livestock, and the whole environmental biodiversity [29]. They are known to be carcinogenic and potentially threaten the environment and the living [5,30,31]. Due to its toxicity to humans, some of these dyes are listed among the benzidine-based dye by the U. S. Environmental protection Agency (EPA) .

The excessive use of these dyes leads to their release of a significant amount of its effluents into the environment, especially the water bodies [24]. It was reported that 10-15% of the total dye consumed in the dying process in the textile industries is being lost to the environment. Subsequently, this massive amount of dye effluents cause severe concerns to the water bodies. It compromises the aesthetic color of the water bodies and impaired the biological oxygen demand (BOD). In 2013, it was reported that over $7x10^5$ tons of synthetic dyes are produced yearly, and azo dyes constitute more than 60 to 70% of the total global production of organic dyes. A tremendous amount of water is being used in the textile dyeing and finishing process. Textile dyeing effluent is classified as one of the most adulterating effluents of the industries [32]. The effluent is usually high in both organic and inorganic compounds. Yet, there is still high demand for textile production for various uses globally, making the textile industry one of the biggest industries in the world [26,33].

When released into the environment, dyes are toxic, recalcitrant, and bioaccumulated. There was serious concern on the potential of human carcinogenicity and mutagenicity on the exposure to Azo dyes. That is why there are strict regulations and control of dye used in many developed countries. Furthermore, metabolites of these dyes and their congeners (e.g., aromatic amines) are documented to be toxic, carcinogenic, and mutagenic to humans [5,34]. They react with the DNA and cause mutations.

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Some of these dyes are classified to be highly or non-highly hazardous, and exposure to these dyes could cause symptoms such as eye irritation, diarrhea, respiratory challenges, vomiting, cyanosis, nausea, profuse sweating, mental confusion, methemoglobinemia, jaundice, dyspnea, convulsions, and tachycardia [18,32]. Some are linked to hepatocarcinoma, splenic sarcomas, human bladder cancer in exposed dye workers, and liver noodles in experimental animals. Therefore, dyes demand extensive treatment before being discharge

The European Union has successfully traceback the contamination of several dyes in several exposed environments from textile processing industries [35–37]. These dyes and their metabolites pass through the food chain from the contaminated environment (water or soil) and cause serious human health concerns. Research conducted on rats has proved Trypan Blue dye to be a carcinogenic substance. After administration, it produced reticulum cell sarcomas of fibrosarcomas and the liver at the injection site. Biodegradation of Azo dyes has been notorious for its enhanced mutagenicity and recalcitrant to several microorganisms because of the aromatic ring structure. At this time, there are several significant efforts to develop clean, cost-effective, and environmentally friendly treatment technology to effectively remove dye pollution from the environmental sink [28].

Global account of dye incidences

The textile industry has been among the world's largest sectors in terms of employment and productivity. In the U.S, dye production has been slowly declining over the years, owing to the increase in imported finished textiles from countries such as India, China. Developing countries with fewer strict restrictions on dye production and uses [38]. It has a forecasted year market size of USD13.6 billion. The European Union ban on the use of some of these dyes has been very strict; that is why there is none of the List 1 dye incidence reported in the U.S. in 2006 [24]. However, only 12 of the List 2 are believed to be available. In Bangladesh, the textile industry is a mix of small and large scale companies, and more than four (4) million out of the country's overall population are involved in the dye production, with women accounting for the majority [39]. The industry is said to provide 45% of employment in the industrial sector. The most prominent dye and dye product hubs in Bangladesh include Dhaka, Chittagon, Khulna, Narayanganj, Gazipur, and Dinajpur. In India, the textile industry is the country's first and most prominent. It accounts for up to 17% of its overall export. India's textile industry was reported to provide job opportunities for 35 million people across the world [39]**.** Textile/dye hubs in India include Bangalore Panipat, Ahmedabad, Coimbatore, Ludhiana, and Tirupur.

Similarly, Pakistan's textile industry has played a positive and significant part in the country's gross economic activities. In the Asian region, Pakistan is ranked 8th highest exporter of textile products, contributing meaningfully to the country's export, and the sector contributes 8.5% to the total GDP. It employs approximately 15million people. Dye and dye products hubs in Pakistan include Lahore, Karachi, and Faisalabad [38].

Conventional methods for dye removal

Because of the complex molecular structure of the Azo dyes, it has been challenging to remove the dyes from the effluents. They are generally stable to heat, oxidizing agents, and lights. Different technologies are seldom used to remove dyes from effluents, such as coagulation, oxidation, flocculation, ion exchange, chemical precipitation, photocatalyst, membrane filtration, and activated carbon sorption. Membrane filtration uses pressure to remove the dye contaminants from effluents, but its major drawback is sludge production [38,40]. At the same time, activated carbon has been regarded as a relatively effective method for the treatment of dye effluent, but it is expensive. In reverse osmosis, the effluent is forced through a semipermeable membrane which traps the contaminating solute while allowing the water to flow; however, its cost is one of its significant drawbacks. Ion exchange has been a popular technique but has its drawbacks, such as incomplete removal of some ions and high cost. The chemical precipitation technique involves the use of coagulants, e.g., alum, iron salts, or lime, to achieve precipitation, but this produces a large volume of sludge containing toxic compounds [41,42].

Several factors affect the overall process of the conventional dye removal methods, such as flexibility and simplicity. Unlike biomass-based removal techniques, these conventional methods are highly selective and expensive to operate [16,43]. As mentioned earlier, some of the drawbacks, low dye removal capacity, accumulation of toxic sludge, high requirements of energy, and reagents, are justification for alternative cost-effective biological solutions.

Biosorption

Biosorption is the process in which biological materials (dead or living) are used to remove chemical substances (organic or inorganic) from a solution. Adsorption is the physical adherence of molecules/ions onto another molecule, while absorption is the assimilation of substances from one phase to another [44]. The process of biosorption involves the liquid (sorbate) and solid (sorbent) phases. Therefore, biosorption can be defined as a physicochemical remediation process in which biomass (dead/inactive) concentrates and binds pollutants onto its structure [45,46], while bioaccumulation uses living cells, biosorption uses dead biomass. The process involves different mechanisms such as adsorption, absorption, surface complexation, precipitation, and ion exchange. Numerous factors have been identified to significantly affect the biosorption of different biosorbents. These factors include contact time, pH, ionic strength, temperature, and contaminant concentration [2].

Since in the 18th and 19th centuries, the ability of microorganisms to adsorb metals from solution has been studied. However, in the last few decades, non-living microorganisms are started to be used as absorbents to remove and recover materials from aqueous solutions [28,45]. Waste and sewage disposal are the very first materials used for the implementation of the biosorption technique [47]. In 1973, Ames Crosta Mills and Company Ltd. Received the first patent for biosorption apparatus [26]. Over the years, several technologies have been known for the removal of dyes from the environmental sink [48,49]. Different technologies including physicochemical, biological processes, or both, are used. Examples of physicochemical methods are ion exchange, activated carbon adsorption, photochemical process, electrochemical oxidation, sonication, photocatalysis, membrane separation, coagulation or flocculation, ozonation, etc. Another viable dye adsorption method is the use of adsorbents such as agricultural and as well as industrial wastes (e.g., fly ash, activated carbon, plant biomass, fermentation waste from the industries); however, the release of the adsorbed dyes is an environmental concern.

Wastewater containing dyes are challenging to treat because of their recalcitrant nature, stability to oxidizing agents, presence in trace amounts, and resistance to aerobic digestion [45,50]. In essence, all the methods shown above have their advantages and disadvantages [45]. That is why there is an urgent need to develop

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cost-effective and environmentally friendly dye removal and detoxification alternatives [51]. The adsorption method has been identified to have upper advantages over most conventional methods because of its simple design, high efficiency of dye removal, cost-effectiveness, ease, and quick process [34,52]. Also, it can be used to treat effluents from both organics and inorganics. More so, the sludge yield from the adsorption process can be used to produce activated carbon [35,44,53].

Advantages of Biosorption using non-living cells

i- There is no requirement for costly nutrients to maintain the sorption process, and there is no physiological constraint of living microbial cells.
ii- Since biomass is non-living, there is no limitation of toxicity on the cells.
iii- Biomass can be procured from existing agricultural, fermentation, or industrial waste.
iv- The process is usually fast (take place within minutes to hours). This is as a result of the characteristics of biomass which behaves as an ion exchanger.
v- Because the cells are non-living, the process does not generally require aseptic conditions.
vi- Biosorbates uptake can be mathematically modelled more easily.
vii- Easy regeneration and reuse of biomass.

Disadvantages of biosorption using non-living cells

i- Since the cells are not metabolizing, there is no room for biological enhancement of the cells, e.g., genetic engineering of the cells.
ii- There could be biomass saturation challenges in up taking the dyes during the adsorption process.
iii- Recycling of biomass after adsorption.

Mechanism of dye removal by biosorption

Biosorbents are derived from different raw biomass such as plants, fungi, yeast, algae, and bacteria. The mechanisms in which these biosorbents remove dyes (biosorbates) vary in different ways, and this is because of the complex nature of varying biomass. Although, some of these mechanisms are not yet well understood. Dye's biosorption mechanism is generally attributed to the structure and functional aspects of the extracellular polymeric substance of the biosorbents [37,54,55]. Based on the biosorbent used, different functional groups attract or insulate the dye pollutants. Examples of the functional groups found on the biomass include carboxyl, sulfonate, amide, carbonyl, amine, imine, sulfhydryl, phenolic, imidazole, phosphodiester, and phosphate groups [56].

Several specific factors determine the significance of these groups for the biosorption of dye pollutants by given biomass. These particular factors are the site availability (site functional chemical condition), binding strength or affinity between a given dye and the site, and the number of the reactive sites of the biosorbent [17,57]. Therefore, the existence of some of these functional groups will not guarantee an effective dye biosorption when conformational, a steric, or any obstructions exist. Dye biosorption is primarily mediated through chemisorption, surface adsorption, adsorption complexation, and diffusion [50,58]. Most importantly, pore diffusion, film diffusion, and chemical reactions such as complexation and ion exchange [59,60]. In the biomass-dye system, interactions (intermolecular) are most likely, with the amine site being the most reactive group, accompanied by the hydroxyl group.

Ion exchange

Dye wastewater often has high metal ions, which might impact biosorption rate and capacity by acting as bridges in the biosorption process. Ion exchange is a reversible process in which an ion is being substituted by another with a similar charge in an insoluble solid phase in a solution. In detail, it is the exchange of an absorbed ion by another [61,62]. This technique is mainly used for the purification or separation of an aqueous solution. This mechanism has successfully been seen in the removal of metals and dyes from industrial effluents [63]. According to Mahony et al., [64], the presence of 100 mg L^{-1} Cd^{2+} ions reduced the absorption of reactive dyes owing to competition between Cd^{2+} and dye molecules. According to Liu et al., [65], the addition of metal ions to the lyophilized biomass of *B. megaterium* did not affect dye removal. The percentage removal are 96, 93, 94, 92 and 92% in a solution containing Calcium Ca^{2+}, Potassium (K^{+}), Magnesium (Mg^{2+}), Sodium (Na^{+}) and Cadmium (Cd^{2+}), respectively . Furthermore, ion exchange is a nonselective process that is very susceptible to the pH of the solution [66].

Precipitation

This a process in which a soluble chemical substance is being transformed into a solid form. Precipitation, in which bound metal/radionuclide species serve as loci for eventual deposition, can result in higher absorption capacities, but it can also prevent desorption [41,63]. According to Wang et al., [67], Cadmium adsorption onto feedstock-derived biochar occurred mostly owing to precipitation or cation exchange processes. Also, Huang et al., [68] reported the adsorption processes of Cadmium onto magnetic graphene oxide as metal hydroxide precipitation, isomorphic exchange, and complexation with functional groups. However, a full investigation of the adsorption processes is currently being investigated.

Complexation

Complexation or coordinate complex is an array of bound molecules/ions surrounding that are known as ligands. It is made up of a central ion or atom, which usually is metallic. These complexes are found in many metal-containing compounds [69]. It may be electrostatic or covalent. Mechanisms and reactions of coordination complexes are represented in so many ways, which can be confusing [63]. The donor atom (atom in the ligand) is the atom bound to the central metal atom or ion. In a given complex, a metal ion is bound to multiple donor atoms that may be the same or different. A multiple bonded ligand is an ion or molecule that attaches to the central atom by some of the ligand's atoms [47]. The term used to describe these complexes is complexation, chelation, and coordination.

Chelation

This is a process in which molecules and ions are bonded to metal ions. Between the multiple bonded (polydentate) ligand and single central atom, two or more different coordinate bonds are formed. Chelation has also been termed as the process of forming complexes with multidentate ligands [50]. Many studies have realized and described that the biosorption process can be independent or combined with electrostatic interaction, ion exchange, precipitation, chelation, and complexation processes. The method works by partly dissolving dye molecules in textile wastewater and then leaving the hazardous residues in the effluents [70].

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Factors affecting biosorption

Several factors have been known to affect the biosorption of dyes. Some of these important factors include; temperature, biosorbent dosage, pH, agitation speed, ionic strength, initial solute concentration, type, and nature of the biosorbents [50,71]. More so, physical treatments such as drying, boiling, mechanical disruption, autoclaving are all found to affect the binding properties. Others include the surface area to volume ratio, biomass concentration, and pollutant solubility. Many pieces of literature reported that the solution pH plays an important in biosorption. It affects the solution chemistry and as well the activity of the functional groups of the biosorbents. In addition, dye biosorption depends on the solution pH in different biosorbents systems, including bacteria. Probably, of all other factors pH, is the most critical biosorption factor [59,72].

Effect of pH

The pH influences the chemistry of the solution, the functional groups' behavior of the biomass, and creates competition with coexisting ions in the solution. The pH has been termed as the most important regulator of biosorption [13,50]. If the pH is increased, it enhanced the removal of cations or basic dyes while reducing the anions of metals or acidic dyes [72]. Generally, the biosorption capacity is flawed at a low pH value and rises with increasing pH value until it reaches an optimum pH value.

Liu et al., [65] studied the adsorption of Reactive Blue 5 by pH-independent lyophilized biomass of *Bacillus megaterium* in an aqueous solution and found out that reactive blue 5 could not be completely ionized into negatively charged dye anions. On the other hand, carboxyl and amine groups found in *B. megaterium* contributed to the reactive blue 5 biosorption process. They adjusted the pH from 2 to 11 using HCl and NaOH. The adsorption was performed at 28 °C for 18 hours and the removal was above 85% with a slight difference within the pH range 2 to 11. Other studies reported that bacterial cells had the best ability (90%) for removing reactive blue 5 at pH 3, whereas at pH 5 and 11, dye absorption levels declined to almost 50% and 10%, respectively [65]. However, according to Wang et al., [67] high dye absorption values at low pH can be attributed to electrostatic interactions between negatively charged dye anions and positively charged biosorbents.

Effect of agitation rate

It was shown that an increase in agitation speed increases the biosorption rate of the dye. However, the rate of the agitation speed was found to damage the biosorbents structure in some cases [73–75]. The agitation speed provides proper contact between the sorbate and the sorbent, that is to say, the solution ions and the binding site of the biomass. It reduces the surface mass transfer barrier thickness surrounding the adsorbent particles, allowing efficient sorbate ion transport to the sorbent sites. It was demonstrated that increasing the rotating speed enhanced the removal efficiency until it reached a maximum, followed by a decrease in sorption capacity at higher agitation speeds [76].

Several findings revealed that interaction between solid and liquid is more successful at moderate agitation (150 rpm), providing the best homogeneity for the combination suspension [6]. The decline in effectiveness at higher rotating speeds may be related to inappropriate contact between solution ions and binding sites, as the solution is no longer homogeneous due to vortex formation, making adsorption harder [76,77].

Effect of temperature

Generally, biosorption removal of dye is enhanced with an increase in temperature [77,78]. This increases kinetic energy and the surface interaction of the dye with the biosorbent. This may also have a damaging effect on the structure of the biosorbent [36]. Temperature is an important physicochemical process parameter because it changes the adsorption capacity of the adsorbent. An Adsorption is said to be endothermic if the number of adsorption increases as the temperature rises. This might be due to the dye molecules being more mobile and the number of active sites for adsorption rising as the temperature rises. Whereas, when the temperature rises, the adsorption capacity decreases, indicating that adsorption is an exothermic process. This might be because when the temperature rises, the adsorptive forces between dye species and active sites on the adsorbent surface decrease, resulting in less adsorption [28]. Liu et al., [65] investigated the effect of temperature on the adsorption of Reactive Blue Red and found out that the process was endothermic. In another study, Cherfi et al., [77] reported that adsorption is favoured at a high temperature. Therefore, in an adsorption study, it is necessary to optimise the effect of temperature because of the variability with seasons and regions.

Effect of biosorbent dosage

The biosorbent dosage heavily influences the extent of biosorption. In many instances, lower biosorbent dosages result in higher uptakes [79]. However, an increase in surface area increases the number of the binding sites of the biomass, which in turn increases the volume of the dye absorbed [9]. This is not favorable when using the column biosorption process because of clogging of the column and lower mechanical strength. Due to the dynamic interactions of many factors, an increase in biomass dosage results in a decrease in dye per unit weight uptake [13,57]. The dye solute is insufficient to cover the available exchange site of the biomass, which results in low dye uptake.

Effect of other co-pollutants

When co-pollutants compete for binding sites with the primary pollutant, it will reduce the biosorptive removal of the target pollutant [37]. These co-pollutants can equally create complexes that reduce the removal of the target pollutants [1]. In contrast to controlled laboratory circumstances, industrial effluents contain a variety of contaminants, including the target pollutant of interest. Increased concentrations of other pollutants (s) will decrease biosorptive removal of the desired pollutant(s). As a result, research into the inhibitory effects of ionic strength and competing ions is required. Since the biosorption process takes place mainly on the surface of the biomass, changes to its surface can have a significant impact on its biosorptive capacity and function. To decrease the influence of additional co-pollutants, particularly metals, a variety of chemical, physical, and other treatment approaches have been used [17].

In certain circumstances, a target chemical group found in biomass will be chemically changed in order to define the biosorption process associated with that group. Physical or chemical activation of raw biomass for transformation into chars or activated carbons is an excellent example of this. Physical modification is often easy and affordable, although it is less successful than chemical modification. Chemical pre-treatment (washing) has been chosen over other chemical modification approaches due to its simplicity and efficiency.

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Acid-washing can improve the capacity of biosorbents for cationic metals or basic dyes in many circumstances by extracting soluble organic or inorganic constituents from raw biomass and/or modifying its biochemistry [74]. Some chemicals, on the other hand, might cause significant mass losses in the biosorbent (i.e. structural degradation) as well as a decrease in biosorptive ability. The augmentation or alteration of a biosorbent's functional groups can result in significant changes in its biosorptive ability. Amine, carboxyl, hydroxyl, sulfonate and phosphonate groups are recognized metal or dye-binding sites; consequently, these groups can be freshly generated or their levels raised to improve biosorptive ability [69,74].

Finally, in instances when microbial biomass is used, the biosorptive capacity can be increased by adjusting growing conditions or applying genetic engineering approaches at some point of development. Genetic modification might be possible, particularly if genetically altered microorganisms were included in the fermentation process. In conclusion, the above-mentioned techniques may be used to create effective biosorbents from diverse raw biomass types. However, the economic cost of the biosorbents rises as a result of the alterations, putting them closer to the cost range of man-made ion-exchange resins. It should not be overlooked that the primary benefit of biosorbents is their inexpensive cost in comparison to commercial adsorbents such as ion-exchange resins.

Effect of initial dye concentration

If the dye rises, the amount of dye adsorbed per unit weight of biosorbent rises and hence reduced the removal efficiency [7,80]. The quantity of dye removal adsorption is strongly dependent on the original dye concentration. The influence of initial dye concentration is determined by the direct relationship between dye concentration and accessible sites on a surface of the adsorbent [81].

In general, when the initial dye concentration increases, the percentage of dye removal decreases, which may be due to the saturation of adsorption sites of the adsorbent. On the other hand, an increase in initial dye concentration will increase adsorbent capacity, which may be related to the strong driving force for mass transfer at an increased initial dye concentration [28]. Zhang et al., [82] investigated the adsorption of Methyl Orange by the Chitosan/Alumina interface and discovered that when the Methyl Orange grew from 20 mg/L to 400 mg/L, the percentage of dye removal reduced from 99.53 percent to 83.55 percent with the same MB concentration range. Furthermore, Velkova et al., [79] studied the Biosorption of Congo Red and Methylene Blue by pre-treated waste *Streptomyces fradiae* biomass and reported that the biosorption capacity was increased as the original dye concentration rose, because of the strong driving force for mass transfer. Also, the removal effectiveness decreased with increasing concentrations of MB and CR owing to saturation of the binding sites on the adsorbent surface.

Bacterial biosorption of dyes

In recent, bacterial use as a biosorbent has attracted the interest of many researchers as a potential option for dye removal. This was clearly because of the bacteria's quick life cycle, ability to thrive on different substrates, can grow in optimized conditions, and production of less harmful byproducts. Bacteria are a large group of unicellular living organisms common in the soil, water, and symbionts on many other organisms [9,83]. They are a significant portion of the ecosystem and, therefore, known as cosmopolitan organisms.

They have different types of shapes and ranges in sizes. Generally, two types of bacteria exist, Gram-positive and Gram-negative. Gram-positive have a thick layer of peptidoglycan, while Gram-negative have a thin layer [36]. The Gram-positive bacterial cell wall comprises 90% peptidoglycan while Gram-negative is only about 10-20%, and the remaining percentage, phospholipids and lipopolysaccharides [20]. The peptidoglycan determines the bacterial cell wall structure, which is responsible for its rigidity and shape. It is seen as an impermeable barrier to a small substrate, although relatively porous. The bacterial cell wall structure is one of the essential factors in the study and differentiation of the bacterial species. In the bacterial cell wall, functional groups such as amine, carboxyl, and phosphate make up the peptidoglycan [28,84].

The Gram-negative bacterial cell wall has an average negative charge because of the presence of powerfully charged lipopolysaccharides [16,50]. The anionic functional groups found in Gram-positive bacteria's peptidoglycan, teichuronic acids, teichoic acids, Gram-negative phospholipids lipopolysaccharides, and peptidoglycan were found to be the components responsible for the cell wall anionic character and binding capacity [35,50]. In an adsorption setup, when the bacterial cell wall comes into contact with the dye or ions, the solutes are sorbed on the surface or within the cell wall structure of the bacterial biomass [14]. Different parameters, such as temperature, pH, and initial dye concentrations, all significantly impact the dye binding to the bacterial biomass [85]. An essential advantage of using bacterial biomass in biosorption is that waste of bacteria biomass from the food and pharmaceutical industry can be used as inexpensive and readily available biosorbents [19]. **Table 1** below shows numerous works on the biosorption of different dyes using bacterial biomass under different optimum conditions.

Advantages of biosorption using bacterial biomass

i- The procedure is simple in its design, rapid and efficient.
ii- Cost-effective compared to other conventional methods, with no need for expensive nutrients to grow the bacterial cells for biosorption.
iii- It uses a very minimal volume of chemical reagent and does not produce toxic metabolites.
iv- Waste bacterial biomass can be obtained from fermentation industries and be used for biosorption.
v- There are no constraints on living cells, and aseptic conditions might not be essential.

Disadvantages of biosorption using bacterial biomass

i- There is a limitation for possible biological process enhancement, e.g., by genetically engineering the cells. In order words, there is no biological control on the biosorbent since the biomass is non-living cells.
ii- Final disposal of the bacterial biomass has been a significant concern since biosorption is the transfer of sorbate from one medium to another.
iii- Biosorption is compared chiefly with ion exchange; thus, there is concern regarding the specificity of ions or the functional groups.

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Table 1. Adsorption of dyes using different bacterial biomass under different optimum conditions.

Adsorbent (bacterial biomass)	Sorbate (dye)	Initial dye concentration (mg/L)	Contact time (min)	Adsorbent dose	Temperature (°C)	Agitation speed (rpm)	pH	Dye removal	Reference
Rhodopseudomonas palustris 51ATTA strain	Fast Black K	25-400	1440	1 g/L	25, 35 & 45	10 rpm	2-10	25-72%	[86]
Rhodopseudomonas sp. strain 51ATA	Astrazon Red	50-200	1440	1 g/L	25, 35 & 45	-	2-10	4-25%	[71]
Pseudomonas sp. strain MM02	Trypan Blue (TB)	15	20	1.10 g	30	150	6.5	59%	[87]
Bacillus sp.	Brilliant Red HE-3B	8 g/L	1440	0.2 g	20	-	3	88.235 mg/g	[88]
Cyanobacteria	Methylene blue (MB)	50	180	0.2 – 1.5 g/L	25	150	6	85%	[89]
Nostoc linckia HA 46	Reactive Red 198	100-500	120	0.1 g/5mL	25-45	120	2-6	94%	[80]
Corynebacterium glutamicum	Reactive Black 5 (RB%)	500	720	0.1g/40 mL	25	160	1-6	146 mg/g	[90]
Rhodococcus erythropolis AW3	crystal violet (CV)	50	90	0.5 g/L	25	200	9	93%	[83]
Aeromonas hydrophila RC1	Trypan Blue	20-80	60	1.5 g/L	35	-	2-10	46%	[21]
Aeromonas hydrophila RC1	Eriochrome Black T	20-80	90	1.5 g/L	35	-		65%	[21]
Aeromonas hydrophila RC1	Acid Red	20-80	90	1.5 g/L	35	-		45%	[21]
Pseudomonas sp. strain DY1	Acid black 172	100-1000	60	0.05 g	4-100	-	3-9	2.98 mmol/g	[70]
Bacillus megaterium	reactive blue 5	100-400	1080	0.05 g	28-50	150	2-11	94%	[65]
Flavobacterium mizutaii	napthol blue black & direct red 80	-	1440	100 mg	35	120	1-6	250 & 440 mg/g	[73]
Acidithiobacillus thiooxidans	sulfur blue 15	200-2000	20-30	0.38-0.76 gg L	30	200	8.3	87%	[91]
Bacillus cereus M[1]	Malachite green	50-700	360	0.5 g/L	20-50	-	5	485 mg/g	[92]
Pseudomonas guariconensis	Reactive Red 120	100	60	-	-	-	-	91%	[93]
Corynebacterium glutamicum	Reactive Blue 4 (RB 4), Reactive Orange 16 (RO 16), and Reactive Yellow 2 (RY 2)	0-5000	1440	10g/l	-	160	1-10	-	[17]
Bacillus subtilis HAU-KK01	Congo red	100	600		25	0-150		84.5%	[94]
Paenibacillus macerans	Acid Blue 225 (AB 225) and Acid Blue 062 (AB 062)	50-300	10-180	1 g/L	25-55	200	1-10	95%	[95]
Bacillus thuringiensis (Bt) 016	methylene blue	5-25		1 g/L	30	160	2-9	95%	[96]
Streptomyces fradiae	Congo Red (CR) and Methylene Blue (MB	25 to 200 mg dm^{-3}	120	2 g dm^{-3}	298 k	250	2-8	97%	[79]

Adsorption kinetic models and isotherms

Mathematical models have been employed in an effective quantitative way to predict and compare the binding capacities/strength and design of biosorption processes [97,98]. Modeling helps in understanding biosorption dynamics, predicting responses, optimizing biosorption processes, and analyzing results [99–101]. These models (Kinetics and Isotherms) play a significant part in transferring technology from the laboratory to the industrial scale [72,102]. In detail, kinetics explains the rate of dye adsorption, while isotherms describe the equilibrium relationship between the concentrations of the sorbent and the adsorbent phase at a constant temperature [44]. Therefore, to understand and optimize the use of adsorbent and sorbent interactions, adsorption kinetics and isotherm studies are categorically essential [60,102,103]. It provides basic information on the equilibrium adsorption studies on a given system. The sorbent is allowed to achieve equilibrium with the sorbate, and the equilibrium value of the uptake by the biosorbent (q_e) is plotted against the final sorbate concentration (C).

These can be used to compare the capacity of different biosorbent and their affinities. Biosorption kinetics and isotherms have been considered suitable approaches for assessing biosobent capabilities [101,104,105]. Examples of widely used biosorption kinetic models are the Pseudo-first-order, the Pseudo Second-order and Elovich (**Table 2**), while the isotherm models were Langmuir, Freundlich, Temkin, BET, etc. (**Table 3**) [41,94,101]. The Langmuir equation is being utilized to explain the equilibrium between the adsorbent and sorbate in a given system [60,91]. This isotherm model assumes that adsorption energies on adsorbent surfaces are uniform. More so, it is assumed that the adsorbate is covered in a monolayer at the adsorbent's outer surface, with all sorption sites being equal. An essential characteristic of Langmuir is that it can be expressed in terms of dimensionless constants [28].

Table 2. Widely utilized kinetic models.

Model	Equation	Reference
Pseudo-1st order	$q_t = q_e(1 - e^{-K_1 t})$	
Pseudo-2nd order	$q_t = \frac{K_2 {q_e}^2 t}{(1 + K_2 q_e t)}$	[55]
Elovich	$q_t = \frac{1}{\beta ln\alpha\beta} + \frac{1}{\beta lnt}$	[106]

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Table 3. Widely utilized isotherm models.

	Model	Formula	Ref
Single-parameter model			
1	Henry's law	$q_e = HC_e$	[107]
Two-parameter models			
2	Langmuir	$q_e = \frac{q_{mL} b_L C_e}{1 + b_L C_e}$	[108]
3	Freundlich	$q_e = K_F C_e^{\frac{1}{n_F}}$	[88]
4	Dubinin-Radushkevich	$q_e = q_{mDR} exp\left\{-K_{DR}\left[RTln\left(1+\frac{1}{C_e}\right)\right]^2\right\}$	[109]
Three-parameter models			
5	Sips	$q_e = \frac{K_s q_{mS} C_e^{\frac{1}{n_S}}}{1 + K_s C_e^{\frac{1}{n_S}}}$	[110]
6	Toth	$q_e = \frac{q_{mT} C_e}{\left(K_T + C_e^{n_T}\right)^{n_T}}$	[111]
7	BET	$q_e = \frac{q_{mBET} \alpha_{BET} C_e}{(1 - \beta_{BET} C_e)(1 - \beta_{BET} C_e + \alpha_{BET} C_e)}$	[112]
Four-parameter models			
8	Baudu	$q_e = \frac{q_{mB} b_B C_e^{(1+x+y)}}{1 + b_B C_e^{(1+x)}}$	[112]
9	Fritz-Schlunder-IV	$q_e = \frac{A_{FS} C_e^{a_{FS}}}{1 + B_{FS} C_e^{b_{FS}}}$	[113]
Five-parameter models			
10	Fritz-Schlunder-V	$q_e = \frac{q_{mFS5} K_1 C_e^{\alpha_{FS}}}{1 + K_2 C_e^{\beta_{FS}}}$	[113]

In contrast, the Freundlich isotherm model describes the sorbent surface as a non-uniform system that the adsorption surface possess were varying sites with different affinities [7,79]. The equation was firstly proposed for the adsorption of the gas-solid interface [28]. Tempkin describes the uniformity of the adsorption system owing to the sorbate–adsorbate interactions. The heat of adsorption of all molecules in a layer decreases linearly with adsorbent surface distribution [37,95,114]. The BET isotherm describes multilayer adsorption at the adsorbent surface, assuming that each layer follows the Langmuir equation [35,57]. Another presumption is that a layer does not need to be entirely constructed until the next layer can be formed. Selecting a Kinetic or an isotherm model for biosorption data is mostly dependent on curve fitting goodness, which is usually assessed using statistical analysis [35].

Fitting biosorption data

This involves using electronic software such as Curve-Expert, GraphPad to evaluate the experimental data through statistical analysis [3,115]. The parameters for selecting kinetic or an isotherm equation for biosorption data are primarily dependent on curve fitting goodness [35]. Although, a good curve fitting in the sense of mathematical assessment does not always suggest that it has actual physical meaning. The mathematical curve fitting does not give information about the adsorption mechanisms, and there are generally regarded as simple numerical relationships [116]. Before any chemical importance is assigned to isotherm parameters, experimental proof is necessary. More so, these parameters are only acceptable under the conditions in which the experiment is conducted. Therefore, the collection of kinetic or isotherm equations should be dependent on the mechanism [41]. Instead of simple curve fitting, models with solid theoretical attributes are required to formulate mathematical expressions for biosorption. **Table 4** presents kinetic and isotherms parameters of bacterial biosorption of some dye.

Table 4. Kinetic and isotherm models of bacterial biosorption of dyes.

Adsorbents	Dye name	Kinetic model	linear or non-linear	Isotherm model	Ref
Flavobacterium mizutaii	Naphthol Blue black	Pseudo 2nd order	linear	Langmuir, Temkin	[73]
Flavobacterium mizutaii	Direct Red	Pseudo 2nd order	linear	Langmuir	[73]
Pseudomonas sp. strain MM02	Trypan Blue (TB)	pseudo-second order	non-linear regression	Sips	[87]
Developed bacterial consortium	Reactive Green-19	first-order kinetic	linear	-	[105]
anaerobic sludge -	methyl orange	Pseudo-first-order kinetics	-	-	[101]
Rhodopseudomonas palustris 51ATA	Fast Black K salt	-	linear	Langmuir, Freundlich, and Temkin isotherms	[86]
Bacillus cereus M1	Malachite green	Pseudo second-order	linear	Langmuir and Redlich–Peterson isotherm	[92]
Cyanobacteria sp.	Methylene Blue (MB)	pseudo-second-order	-	Freundlich	[89]
Enterococcus faecalis strain ZL	Acid Orange 7 (AO7)	first-order kinetic	-	-	[117]
Aeromonas hydrophila RC1	Trypan Blue Acid red 26 (AR) Eriochrome Black T (EBT)	first-order kinetic	linear plot	Langmuir	[21]
Bacillus sp.	Reactive dyes		non-linear regression	Langmuir	[88]
Rhodococcus erythropolis AW3	crystal violet (CV)	PSO model	-	Langmuir model.	[83]
Acidithiobacillus thiooxidans	sulfur blue 15 (SB15)	Pseudo-second-order kinetics		Langmuir equation	[91]
Streptomyces fradiae	Congo Red (CR) and Methylene Blue (MB	Pseudo-second order kinetic	linear	Langmuir and Freundlich isotherm	[79]
Bacillus subtilis HAU-KK01	Congo red	second-order		Freundlich	[94]

Bibliometric assessment of literatures on dye biosorption using bacterial biomass

To better reflect the usage of bacterial biomass in dye biosorption, a Scopus keywords search focused on the topics of "dye" "biosorption", "microorganisms" and "dye" yielded 555 journal articles. The VOSViewer sofware is used to create the keyword co-occurrence of the documents, which is displayed in **Fig. 2**. The study's goal is to conduct a complete bibliometric assessment of the research landscape of dye biosorption by bacterial biomass. Four clusters were discovered with the cationic dye Methylene Blue occurring the most often. A significant occurrence of the term "decolorization" together with the term "fungi" and less occurrence with the term "bacteria" indicate a dual approach in the removal of dye from solution especially when fungal biomass is used. The most reported isotherms in descending order were Langmuir, Freundlich, Temkin, Sips, Redlich Peterson and Dubinin-Radushkevich, suggesting that the Langmuir is the dominant isotherms in governing the sorption of dye to bacterial biomass. Of the kinetics model utilized, the pseudo-2nd order occurs more than the pseudo-1st order followed by the intraparticle diffusion and Weber and Morris model.

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The pseudo-2nd order kinetics is more predominantly reported in the literature [118–120] partly due to its mathematical advantage compared to pseudo-1st order [121]. Column studies were the least studied with 12 occurrences with the rest being batch adsorption studies. It appears that in recent years, dye biosorption by bacterial biomass is more often reported compared to yeast and fungal biomasses.

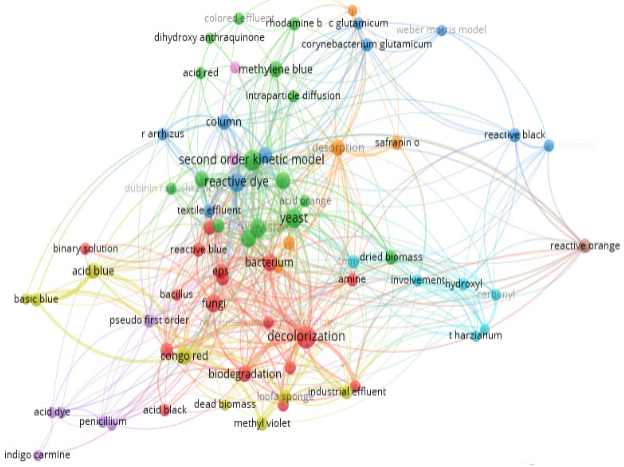

Fig. 2. SCOPUS keywords mapping using VOSViewer software, (Keywords: biosorption, microorganisms and dye).

Thermodynamics

In biosorption studies, thermodynamics study is crucial since it provides important information about the reaction's nature and its feasibility. Thermodynamics parameters include the Gibbs free energy Change (ΔG), Enthalpy change (ΔH), and Entropy change (ΔS) [122]. The thermodynamic parameters were used in defining the difference between physical and chemical biosorption processes. The physical biosorption process exhibits a weak physical reaction, while the chemical biosorption process shows a stronger reaction [60]. Therefore, the response is either physical (physisorption) or chemical (chemisorption) process or a mixture of both mechanisms (comprehensive adsorption) [123]. The effect of temperature on the rate of chemical reaction in biosorption was well documented, which is calculated using the empiric law of van't Hoff's [60,124]. The law states that a 10-kelvin rise in temperature increases from 2 to 4 folds in the reaction time. In detail, an increase in the temperature will reduce the reaction time. Therefore, the overall reaction rate can be experimentally measured at different temperatures [116].

Several studies have reported that an increase in temperature leads to a decrease in the biosorption process, and the process is said to be an exothermic ($-\Delta H$) reaction, heat in the form of energy is released into the environment [77]. In contrast, the reaction is defined as endothermic when energy is gained from the environment, in the form of heat ($+\Delta H$) [79]. In the endothermic process, the total energy released in the bond breaking is less than the total energy absorbed in the bond making between the sorbate and the adsorbent. It is said to adsorbed energy from the environment [60].

The Gibbs free energy (ΔG) is used to assess the spontaneity of the biosorption process [122]. At a given temperature, a higher negative value ($-\Delta G$) indicates a spontaneous biosorption process which is favourable, while in contrast, a non-spontaneous non-desirable reaction process is a positive Gibbs free energy change ($+\Delta G$). This also demonstrates the type of the reaction process, either physisorption or chemisorption [87,89]. The entropy change (ΔS) represents a degree of randomness of the sorbate in the reaction solution. A negative $-\Delta S$ value indicates associative reaction, while a positive $+\Delta S$ value represents dissociative reaction process [15,41].

$$\Delta G° = -RT \ln KL \qquad \text{Equation 1}$$

$$\Delta G° = \Delta H - T\Delta S° \qquad \text{Equation 2}$$

The $\Delta H°$ and $\Delta S°$ values were calculated using slope and intercept of the plot of $\Delta G°$ against T, R is the universal gas constant, and T stands for the solution temperature.

Activation energy (Ea)

It is the minimum amount of energy required to get molecules and atoms into a chemical reaction [60,78]. The activation energy of biosorption (E_a) is calculated using the Arrhenius expression and the kinetic approximate parameters (K_f, D_{ef}, k_a) from phenomenological models as a function of temperature [60,100].

Characterization of bacterial biomass

As the surface morphology of bacterial biomass is subject to changes when interacted with many compounds, several techniques are used to characterize dye biosorption by the bacterial biomass [16,51]. These techniques include Fourier transform infrared (FTIR), Transmission electron microscopy (TEM), X-ray absorption spectropotocopy (XAS), Nuclear magnetic resonance spectroscopy (NMR), Scanning electron microscopy (SEM), Atomic force microscopy (AFM) [19,83].

Transmission Electron Microscopy (TEM) is a microscopic technique in which an image is created by passing an electron beam through a sample or a specimen. On the order hand, Scanning Electron Microscopy (SEM) is a microscopic technique that uses a directed beam of electrons to scan the surface of a sample or spacemen to obtain images [48,96,117]. When the electrons communicate with atoms in the specimen, they provide different signals that give details about the specimen's surface structure and composition. These techniques and many others, such as AFM (Atomic Force Microscopy), are used to characterize dye biosorption by bacterial biomass [51,91]. Generally, specimens or samples (bacterial biomass) are prepared before and after the batch adsorption experiment [63,125]. The samples are being washed, dried, and then coated in some cases. The samples are then analysed using the respective instruments under appropriate resolution at a given voltage, and the micrographs are recorded [58].

A previous adsorption study of bacterial biomass by Anh et al., [91] used Scanning Electron Microscopy (SEM) to examine the surface morphology of the bacterial biomass samples before and after the adsorption. The samples were first dried at 65℃ to a stable weight, then scanned using a scanning electron microscope. From the scanning images, the surface morphology of the biomass was found to be heterogeneous, non-porous, smooth, and tight structure. The images revealed the presence of adhesive binding of the bacterial biomass surface and that of the dye [91]. Another similar study reported adhesive interactions and the presence of ionized functional groups, phosphodiesters, carboxyl, and amino groups on the surface of Gram-negative cells [60,91].

AFM is used to examine surface morphology of biomass or adsorbent, and unlike SEM, it does not require imaging under vacuum, fixation, or conductive coating [17,51]. Equally, TEM reveals all the visible surface morphology of the bacterial biomass (before and after dye adsorption. Fourier Transform

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Infrared (FTIR) spectroscopy is a technique used to obtain an infrared spectrum of a gas, liquid, or solid's absorption or emission [17,105]. The spectrometry technique gathers high-resolution spectral data over a wide range of spectral arrays at the same time [126]. This is an important advantage over a dispersive spectrometer which can only measure sensitivity over a few wavelengths at a time. This technique is widely used in the characterization of biomass in biosorption studies [61]. FTIR is used to reveal the concentration and types of functional groups of cell wall components in the bacterial biomass responsible for the dye adsorption [9,14,63]. Consequently, this data can be used to identify the chemical bonding involved in the adsorption. Bond stretching or bond vibration is referred to as a molecular expansion and compression of the bond lengths [127,128].

A functional group is an atom or bond within a compound which is responsible for the compound's chemical reactions [9,14]. The same functional group can behave similarly and perform identical reactions irrespective of the compound it is contained in [9,63]. Therefore, a functional group can differentiate similar compounds from each other since it functionalizes compounds. In material science, functional groups are being used to achieve desired surface properties where the functional groups can be covalently linked to the surfaces functional molecules of other chemical materials [14,61]. Examples of common organic functional groups include amines (NH_2), carboxylic acids (CO_2H), carbonyls (C=O), phosphate, esters (CO_2R), and hydroxyl (-OH). In detail, the functional groups are referred to as the adsorption sites, and each of the groups produces its own unique adsorption peak of energy in the FTIR spectrum [57].

Although, because of the dynamic nature of the bacterial cell wall composition, sometimes it is difficult to precisely identify the functional groups responsible for the bond stretching vibration. However, FTIR reveals information on the classification of adsorbent surface functional groups of dye adsorption using several bacterial biomass [65,85,86]. FTIR spectrophotometry is used to examine adsorbents (bacterial biomass) within the range of 400 to 4000 cm^{-1} wave numbers [36,129]. Das et al., [73] used the FTIR technique to identify and classify various stretching of the surface functional groups of *Flavobacterium. Mizutaii.* In their finding, the spectra of the bacterial biomass show a solid band at the region of 341.51 cm^{-1}, which suggested a characteristic of O-H or N-H stretching.

Alkyl group band represented by 2920 to 2850 cm^{-1}, amide I was stretched by C=O at 1660.3 and 1634 cm^{-1} band. In contrast, amide II stretching was a combination of N-H bending and C-N stretching, which were centered at 1554.6 and 1526 cm^{-1}. Furthermore, they reported a band at 1459.9, 1446.6, and 1409 cm^{-1}, which was suggested to be of the carboxylate group (COO). The other bands were attributed to the hydroxyl, carboxyl, amine, and phosphate stretching, 1074 and 968. It was observed that there were differences in some of the FTIR signals with a change in pH of the solution, particularly in the range of 2000 to 500 cm^{-1}. Another similar previous study by Anh et al., [91] the appearance of peaks at 3445 cm^{-1} for $-NH_3$ stretching aromatic amine, $-NH_3^+$ deformation at 1643 cm^{-1}, N=O stretching at 1452 cm^{-1}. -SO stretching of sulfide at 1132 cm^{-1}, and -CH deformation at 973 cm^{-1}. The table below shows the characterization of different biomass based on FTIR, SEM, and AFM techniques. **Table 5** shows the characterization of biosorbent and their functional groups.

Table 5. Characterization of adsorbent using FTIR, SEM, and AFM of some dyes.

Biomass	Dye	Type of characterization	Functional groups	Ref
Pseudomonas sp. strain MM02	Trypan Blue	FTIR, XPS and SEM	amino, hydroxyl, sulphonate, carboxyl, and carbonyl	[87]
Cyanobacteria sp.	Methylene Blue (MB)	FTIR, SEM and EDX	hydroxyl, carboxylic acid, amine, amino, sulfonyl and phosphate functional groups	[89]
Acidithiobacillus thiooxidans	Sulfur Blue 15	SEM, and FTIR	Amine, sulfide, amide, and carboxylic	[91]
Flavobacterium mizutaii	Naphthol Blue Black and Direct Red	FTIR, AFM, and SEM	amine, carbonyl, hydroxyl, and phosphate	[73]
Bacillus cereus **M^1_{16}**	Malachite Green	AFM and FTIR	carboxyl, amide nitro, hydroxyl	[92]
Paenibacillus macerans	Acid Blue 225 (AB 225) and Acid Blue 062 (AB 062)	FTIR	carboxylic acid and amino groups.	[95]
Rhodococcus erythropolis **AW3**	Crystal violet (CV)	FTIR, SEM, EDX	hydroxyl, amine, amides, phosphate	[83]

Mechanism of dye adsorption onto inactivated bacterial cells

When a solid surface comes into contact with an aqueous solution or gas, there is interaction between the two-phase system. This is because an adsorptions occurs by unbalanced and unsaturated molecular forces on each solid force. The ions, atoms or particles of the solution have a tendency to attract and adhere to the solid surface. Regardless of the properties, this causes a higher liquid concentration near the solid surface. The process that causes this surface excess is known as adsorption.

Factors found to affect adsorption are, physical factors such as disperse force, polarization force, dipole force while chemical force including the valency force. Adsorption has been classified into physical and chemical sorption due to the nature of forces involved, physisorption or chemisorption [59]. In the case of the physical adsorption, the adsorption force is relatively weak lander wall forces which imitate molecular forces of cohesion. In the alternative, the chemisorption exchanges electrons between adsorbed molecule and the component of the adsorbent. The Chemisorption since it is mediated by chemical reaction is a stronger between the adsorbate and the adsorbent compared to the physisorption.

Chemisorption occurs to a specific adsorbate to adsorbent process while physisorption is unspecific. Generally, the thickness of the adsorbed phase is the most important difference between the physisorption and the chemisorption. in the later, the thickness is unimolecular while in the former, the it is multi molecular. In a given adsorbate-adsorbent process, the kind of adsorption that occurs is determined by the adsorbates' surface area, the adsorption pressure and temperature. There are numerous common terminology used in adsorption studies to describe how the adsorption process occurred. The terms mono-layer and multi-layer, for example, are used to describe the interaction of solids and liquids in an adsorption process. Such terms define the process rather than the layer of the adsorption surface [116].

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Bacteria are mostly employed as biosorbents, because they are ubiquitous and have key properties like size, and can thrive in an ideal settings. Bacteria are classified into two types: gram positive and gram negative [35]. Gram positive bacteria have a thick layer of peptidoglycans, whereas gram negative bacteria have a 10 to 20% thinner layer of peptidoglycans. In the bacterial cell wall, peptidoglycan surface contains functional groups such as amine, carboxyl, hydroxyl and phosphate that's binds to the sorbate ion and molecules [20,130]. These are responsible for the characteristics of binding site and dye attachment. The biosorption process is evaluated by finding the adsorption binding site by functional group changes using FTIR analysis. A higher transmittance value at a frequency implies that the sample has few bonds that absorb light, whereas a low transmittance value suggests that the sample contains a higher number of bonds with vibrational energy that correspond to the incident light. The binding of dyes to bacterial biomass is primarily regulated by several variables, including pH, temperature, and dye concentrations. In several instances, bacteria from the genus *Pseudomonas*, *Bacillus*, *Streptomyces*, *Escherichia*, and Micrococcus were used in removal of dyes [58].

CONCLUSION

Bacterial biomass has been studied for its potential in adsorbing dyes from aqueous solutions. Various bacterial species, such as *Bacillus* sp., *Pseudomonas* sp., *Rhodococcus* sp. and *Aeromonas* sp., have been investigated for their ability to remove different types of dyes, including Reactive Red, Methyl Blue (MB), Malachite Green (MG), Eriochrome Black (EB), Acid Red (AR), and Trypan Blue (TB). In some cases, the adsorption process involves the immobilization of bacterial biomass. The adsorption of dyes occurs through chemisorption, physical interaction, or a combination of both mechanisms. The adsorption capacity of bacterial biomass for dyes can be influenced by factors such as pH, temperature, dye concentration, contact time, agitation speed and biomass concentration. The Langmuir, Freundlich isotherm models have been commonly used to describe the adsorption behavior of dyes on bacterial biomass . Overall, bacterial biomass shows promise as an effective and economical adsorbent for the removal of dyes from aqueous solutions.

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