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# Biosorption of Triphenylmethane (TPM) Dyes by Microbial Biomass: A Review

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#### ABSTRACT

Many organic and inorganic contaminants are present in wastewater and releasing them into receiving waterways causes major environmental problems. The wastewater produced by numerous industries contains a significant number of dyes; this continues to be one of the most serious ecological issues confronting public health. Unfortunately, conventional wastewater remediation methods are incapable of completely removing dyes. Biosorption is the process by which living material removes chemicals from a solution. Organic, inorganic, gaseous, liquid, or insoluble substances are examples of such substances. Absorption, adsorption, ion exchange, surface complexation, and precipitation are all mechanisms involved in this physicochemical process. It is a characteristic shared by both live and dead biomass. Triphenyl methane dyes are a significant category of commercial dyes known for their remarkable color intensity, bright red, green, and blue colors, and low lightfastness on many substrates. In contrast to live biomass, using dead biomass in biosorption is more ideal since the hazardous nature of pollutants does not affect the sorption process. There is also no need to provide nutrients or maintain a growing environment. In addition to these variables, researchers discovered that dead biomass is more efficient than active biomass at absorbing organic contaminants. This review highlighted the toxicity of dyes, principles, and theory of the adsorption process, isotherm and kinetic studies of some microbial biosorbents, and thermodynamic studies of triphenyl methane dyes adsorption.

## INTRODUCTION

The term "biosorption" refers to the removal of chemicals from a solution by use of biological material. Things like these can be gaseous, organic, inorganic, soluble, or insoluble. The physicochemical steps involve sorption, adsorption, ion exchange, complexation of surfaces, and precipitation. Both living and nonliving biomass have this quality [1]. Biosorption, in contrast to biodegradation, has been shown to be an efficient and straightforward approach for detecting and removing contaminants from water, with the added benefit of being able to recover some of those contaminants.

A substantial volume of wastewater containing synthetic colors is discharged by the textile, paper, paint, printing, and cosmetics sectors. Allergies, dermatitis, cancer, and genetic abnormalities are common side effects of most of these dyes. Additionally, they color wastewater streams, which blocks sunlight and reduces aquatic plants' ability to synthesize oxygen through photosynthesis [2]. Textile and dyestuff industry effluents have a high total dissolved solid (TDS), Biological Oxygen Demand (BOD), and alkalinity, making them challenging to treat. There has been a rise in the amount of rules and regulations pertaining to the use of dyes enforced by regulatory bodies in an effort to lessen the negative impact that dye effluents have on the environment [3].

Not only does organic dye pollution threaten the environment, but it also endangers marine and human life on a worldwide scale. There is evidence that these substances or their byproducts are harmful, carcinogenic, and mutagenic. Not only are these dyes harmful to aquatic life, carcinogenic, and non-biodegradable, but even at low concentrations (< 50 ppm), they disrupt photosynthetic processes and have a negative impact on

the water ecosystem [4]. An essential group of commercial dyes, triphenyl methane dyes are famous for their poor lightfastness on numerous substrates, vivid red, green, and blue tones, and exceptional color intensity [5]. Brilliant Green, Bromophenol Blue, Basic Fuchsin, Coomassie Brilliant Blue, Crystal Violet, Cresol Red, Malachite Green, Methyl Violet, Ethyl Violet, Cotton Blue, Pararosaniline, and New Fuchsin are all examples of triphenylmethane dyes. The mitotic poisoning agent crystal violet is known to cause cancer and tumor growth in a variety of animal species, including bacteria, humans, fish, and rats. Both Malachite Green and Methyl Violet have genotoxic interactions with calf thymus DNA, which can cause cytotoxicity in mammalian cells and irritants in the gastrointestinal tract, skin, and ski. [6]. There is still a long way to go before biological processes can be fully utilized to treat colored wastewater. The use of adsorption as a treatment technology for aqueous wastewater is becoming more commonplace. Activated carbon is the adsorbent that is most used and has the maximum power. Its exorbitant price tag, especially in industrialized nations, made it impractical for widespread usage. As a result, scientists sought out cheaper alternatives, and one promising avenue was the use of microbes and their biomass [7]. Because toxic ions and pollutants cannot influence the sorption process, dead biomass is often preferred for use in biosorption over live biomass. Neither the provision of nutrients nor the maintenance of a growth-promoting environment is necessary. Not only that, but studies have shown that dead biomass is far better at absorbing organic contaminants than live biomass [8].

Table 1. Examples of some commercialized biosorption techniques [10].

Commercialized Biosorbent	Family of Biosorbent	State of cell Free/Immobolized	Company	Affinity	Application Equipment
AlgaSORB <sup>TM</sup>	C. vulgaris	Immobolized on silica	Biorecovery systems	Metallic cations an metallic oxoanions	d Two columns operating in series or in parallel.
B.V. SORBEX	S. natans, A. nodosum, Halimeda opuntia, Palmyra pamata, Chondrus crispus, and C. vulgaris	Powder or granules	B.V. SORBEX Inc.	Specific to toxic heav metals	y Fixed bed system, fluid bed system and completely mixed tanks.
AMT-BIOCLAIM <sup>TM</sup>	Bacillus treated with caustic soda	Immobolized in extruded beads polyethyleneimine and glutaraldehyde		Suitable for accumulation of gold, cadmium and zin from cvanide solutions.	n Fixed bed canisters or fluid- bed ne reactor system
BIO-FIX <sup>R</sup>	Sphagnum, peat moss, algae, yeast, bacteria and aquatic flora.	Immobolized in polysulfone	U.S. Bureau of Mines (Golden Colarado)	Selective for toxic heav metals	ſŸ
MetaGeneR				Remove heavy metal fro electroplating and minin waste streams.	m g
RAHCO Bio-Beads	Variety of sources including peat moss	Immobolized within an organic polymer.		Remove heavy metal fro electroplating and minin waste streams.	m Ig

Despite substantial advances in understanding the complicated phenomena and many publications in this field, marketing biosorption technologies remain a developing worldwide market [9]. In the early 1990s, commercialized biosorbents such as Algasorb<sup>TM</sup>, AMT-BIOCLAIM<sup>TM</sup> (MRA), and Bio-fix were marketed. Because of its ability to cling to pollutants on various biological materials, the biosorption technique has been shown to be crucial. The biosorption mechanism differs because different sorbents have different biological resources. Table 1 shows examples of some commercialized biosorption techniques.

## Toxicity of triphenylmethane dyes

The textile, food, cosmetic, and medicinal industries are just a few that extensively use triphenylmethane (TPM) colors. These dves are highly sought after for their colorful and adaptable qualities, but their toxicological characteristics make them a major threat to both the environment and human health. Because of their inert nature, TPM dyes can build up in the environment and pose a threat to aquatic life. Industrial runoff is a common entry point for these pollutants contaminating aquatic environments. According to research, many different kinds of creatures can be severely poisoned by these dyes. For instance, Basic Violet 3 was harmful to the freshwater microorganisms. The toxicity levels were determined by observing how many microorganisms survived when the dyes were added to the media. Basic Violet 3 showed the level of toxicity compared to dyes tested, resulting in an average survival rate of 20.7% at a concentration of 5.0 mg/L. As the dye concentrations decreased, the survival rates of the microorganisms increased, indicating that its toxicity depends on dosage. This research underscores the dangers that triphenylmethane dyes can pose to microbial communities underscoring the importance of carefully managing and regulating these substances in our environment [11].

Triphenyltin (TPT) affects the water plant Lemna polyrhiza also known as duckweed. When present at a level of 5  $\mu$ g/L TPT visibly impacts the growth of Lemna polyrhiza. The concentration where TPT shows half of its effect (IC50) over 8 days was measured at 19.22  $\mu$ g/L. Furthermore, exposure to TPT boosted peroxidase and nitrate reductase activities at concentrations of 2 and 5  $\mu$ g/L while decreasing chloroplast activity. The bioconcentration factors for TPT in *Lemna polyrhiza* were determined to be 4.3 and 10.9 at concentrations of 2 and 5,  $\mu$ g/L indicating absorption and buildup of the substance by the plant. These results highlight the dangers that TPT poses to plant life. [12].

Several researchers looked at the effects of the dye C.I. Direct Blue 218 on water fleas (Daphnia magna) to see how toxic it is. Many of them perished due to the dye, indicating that it poses a threat to these organisms in areas where industrial dye is abundant. This study emphasizes the need to comprehend synthetic dyes' effects on aquatic ecosystems and implement measures to save life from these pollutants. [13].

One of the most popular triphenylmethane dyes, crystal violet, has some interesting side effects. It promotes tumor growth in some fish species and inhibits glutathione S-transferases in rat liver. Because of its carcinogenic and mutagenic characteristics, this dye—which finds widespread usage in veterinary medicine and biological staining—presents

serious health hazards. According to research, Crystal Violet can kill leukemia cells by phototoxicity, but it has far less impact on healthy hematopoietic cells. Researchers have examined how microbes, especially fungi, break down Crystal Violet, which could lead to bioremediation of areas polluted by this color. Nevertheless, the necessity for strict control and remediation measures is underscored by its bioaccumulative nature and durability [14].

By utilizing Daphnia magna, the toxicity of direct dyes complexed with copper was assessed. According to the research, these colors severely damaged the aquatic invertebrates, and their toxicity levels were much more than those of non-metallized dyes. Copper ions, which can intensify the negative effects of the dyes on aquatic life, are responsible for this heightened toxicity. The study highlights the importance of thoroughly evaluating and controlling metallized dyes because their discharge into the environment can devastate ecosystems, especially on delicate fish species like Daphnia magna [15].

Soil invertebrates *Folsomia candida* and *Eisenia andrei* were discovered to have their survival and reproduction drastically reduced by the xanthene dye phloxine B. Significant reductions in plant root growth and invertebrate reproduction were seen in soil eco-toxicity experiments, where Phloxine B remained persistent throughout the testing period. The study emphasizes the importance of doing comprehensive environmental risk assessments for synthetic dyes that can persist in soil ecosystems. Because of their poisonous effects and long half-life, xanthene dyes seriously threaten terrestrial ecosystems [16].

The phototoxic effects of crystal violet on L1210 leukemia cells in vitro and its ability to suppress conidial germination have been demonstrated. Among the many fields that heavily use this triphenylmethane dye are veterinary medicine and biological staining. Crystal violet has practical uses, but its toxicological qualities make it a major health danger. It is a molecule that has raised concerns about its potential to induce cancer and mutations in humans, according to studies. The results stress the significance of creating safer substitutes for Crystal Violet and the necessity of exercising caution when using it [17]. Textiles, personal care products, and even food manufacturing extensively use synthetic organic dyes. However, their extensive use and large-scale manufacturing have resulted in their prevalence in various environmental compartments, including soil and water. of their toxicological characteristics Because and pharmacological activity, these dyes can cause serious harm to both humans and the environment. Because of the harm they can do to aquatic biota and the fact that they are higher-order consumers, keeping tabs on their environmental occurrence is vital. In order to mitigate the effects of synthetic organic dyes, this review stresses the importance of conducting thorough risk evaluations for the environment and creating efficient regulatory frameworks [18].

The central nervous system of mammals is known to undergo extensive degeneration upon exposure to triphenyl phosphite. This substance can cause cellular and axonal degeneration in the medulla and spinal cord, according to studies conducted on mammals. Additional investigation into the effects of triphenyl phosphite on the central nervous system uncovered that it influences several regions such as the cerebral cortex, thalamus, and cerebellum. Exposure to triphenyl phosphite poses serious health hazards, as demonstrated by these results, which emphasize the compound's powerful neurotoxic effects. According to the findings, triphenyl phosphite has the potential to induce serious neurological effects; thus, strict regulation and preventative actions are required to safeguard human health [19].

Bacterial populations, including *Escherichia coli*, can be negatively impacted by textile dye wastewaters. Research has demonstrated that solutions containing textile dye effluents can be sensitized to create transitory oxidants, mainly singlet oxygen, when exposed to sun radiation. Phenols can be photooxidized and bacterial growth inhibited by these oxidants. These results show that when discharged into the environment, textile dyes can cause serious ecotoxicological problems, especially when they undergo photochemical reactions. To avoid damaging microbial communities in aquatic ecosystems, it is crucial to treat and manage textile dye wastewaters effectively [20]. The toxicity of TPM dyes is summarized in **Table 2**.

 Table 2. Toxicity of Triphenylmethane (TPM) dyes to various organisms.

Organism	Triphenylmethane Dye	Toxicity Details	Reference
Freshwater Microbiota	Basic Violet 1, 2, 3	Basic Violet 3 showed the most toxicity with a mean survival rate of 20.7% at 5.0 mg/L.	[11]
Lemna polyrhiza (Duckweed)	Triphenyltin (TPT)	Toxic effect on growth appeared at 5 $\mu$ g/L; IC50 was 19.22 $\mu$ g/L.	[12]
Daphnia magna	C.I. Direct Blue 218	Highly toxic with significant mortality.	[13]
Various microorganisms	Crystal Violet	Inhibited glutathione S- transferases; shown to promote tumor growth in some fish species.	[14]
Daphnia magna	Copper-complexed dyes	Highly toxic; more toxic than unmetallized dyes.	[15]
Soil Invertebrates	Phloxine B	Significant reduction in survival and reproduction of Folsomia candida and Eisenia andrei.	[16]
Human Cells (in vitro)	Crystal Violet	Inhibited conidial germination; phototoxic to L1210 leukemia cells.	[17]
Various Organisms	Synthetic Organic Dyes	Potential environmental hazard; should be monitored for their toxicological properties.	[18]
Mammalian Central Nervous System	Triphenyl Phosphite	Causes widespread degeneration in the medulla, thalamus, and cerebral cortex in mammals.	[19]
Escherichia coli	Various Textile Dyes	Solar irradiation of textile dye wastewaters inhibits bacterial growth due to photooxidation.	[20]

## Principles and theory of Adsorption Process

Adsorption is the process of adsorptive (gas or liquid) molecules binding to a solid surface. In reality, however, adsorption is carried out in a column packed with porous sorbents as a batch or continuous process. Mass transfer effects are unavoidable in such situations. The entire adsorption process includes mass transfer and consists of three phases [21].

- 1. The process by which adsorptive molecules diffuse from an adsorbent's bulk phase to its surface, also called external diffusion.
- 2. Pore diffusion, sometimes called intraparticle diffusion (IPD), is the process by which adsorptive materials travel from the surface into the pores.

3. The adsorption process involves the surface reacting with the internal surface of the sorbent.

There is opposition to the adsorptive at every stage. According to experimental results, the total adsorption rate is given by the total resistance, which is the sum of the series resistances of the three components [22]. The adsorption rate is increased when the resistance of any component is reduced. When contrasted to the first and second steps, the third step is usually very quick, and hence presents less resistance. A sole-rate regulating step is one that controls the total resistance to such an extent that reducing the other two steps by a small amount improves the adsorptive uptake rate. The types of adsorbents and adsorptives, as well as their characteristics and operating conditions, are among the numerous elements that affect transport resistance.

During the adsorption process, the rate-controlling step can change [23]. When the adsorbent is 80% saturated, the control mechanism for dye adsorption on pine sawdust flips from surface reaction to IPD [24]. Two types of interactions are possible between adsorbent and adsorbate: physical and chemical [21]; the former is referred to as physisorption, whereas the latter is referred to as chemisorption. Different from chemisorption, which includes the transfer or sharing of electrons between adsorbent and adsorbate species to create a stronger bond, physisorption is the result of attraction forces between sorbent and adsorbate molecules [25]. Isosteric heat of adsorption values between 5 and 40 kJ/mol often indicate physisorption as the principal adsorption mechanism, whereas values between 40 and 125 kJ/mol highlight chemisorption as the predominant mode [26,27].

An adsorbent's monolayer capacity refers to its ability to hold a single layer of adsorbed species on its surface. When the adsorptive concentration is high, subsequent layers often stack onto the original monolayer due to intermolecular interaction, resulting in multilayer adsorption, which is physical in origin [26]. Surface heterogeneity has a significant impact on adsorption kinetics and equilibrium. Different kinds of adsorption sites, each with its own specific amount of heat, are present in heterogeneous adsorbents, allowing them to bind the adsorbate. Despite its foundation in homogeneous surface sites, the Langmuir isotherm surprisingly accounts for a large variety of adsorption systems, including those with heterogeneous surface features [28].

The equilibrium and kinetic studies are the two main components of adsorption research. Thermodynamics governs the adsorbent's ability to achieve equilibrium regarding adsorptive loading. The adsorption mechanism influences the rate of adsorptive absorption. A wide variety of equilibrium isotherms exist to represent the equilibrium uptake of any target adsorptive, indicating that the adsorption equilibrium has matured. Adsorption kinetics theory, on the other hand, is progressing far more slowly despite its importance in actual applications of a given sorbent. The kinetic isotherm, which is produced empirically by recording the adsorbed amount against time, is the foundation for kinetics research. Kinetic studies create a model that describes the adsorption rate [21].

## Kinetics models in batch adsorption

A kinetic isotherm is a plot of uptake vs. time that depicts adsorption kinetics. Because the shape of this figure represents the underlying kinetics of the process, it is the foundation of all kinetics investigations. Material parameters like adsorbent and adsorbate types and experimental parameters like temperature and pH influence the kinetics [29,30]. To acquire kinetic data, a batch experiment is usually used. It's critical to maintain consistent experimental conditions during batch adsorption [31,32]. The intrinsic kinetics, or chemical kinetics on the adsorbent surface in the absence of transport constraints, should be revealed by the kinetic isotherm. Batch operation is a popular way to investigate intrinsic kinetics. Applying (i) a high agitation speed (reduced film thickness) and (ii) a small particle size (reduced pore diffusion) can easily reduce or eliminate mass transfer effects [33].

The adsorptive uptake per unit mass of adsorbent,  $q \ (mg/g)$  is given by:

 $q = (C_0 - C)V /m$  (Eq. 1)

#### Where;

Co =initial concentration of adsorptive in the bulk liquid (mg/l) C =concentration of adsorptive in the bulk liquid at time t (mg/l) V=volume of the bulk solution (l) and m=mass of adsorbent (g)

## **Pseudo-First Order (PFO) Equation**

Largergren proposed the pseudo-first-order (PFO) equation for adsorption of oxalic and malonic acid onto charcoal in 1898. Its differential form is as follows:

 $dq/dt=k_1$  (qe-q) (Eq. 2)

Where; q= adsorption capacity (mg/g) t=time (min) and k<sub>1</sub>= rate constant (1/min)

After integrating with the initial conditions of q=0 when t=0, equation (2) becomes;

 $\begin{array}{l} q=qe~(1\text{-exp}~(\text{-kt}))~(Eq.~3)\\ \text{The linearized form of the above equation is;}\\ ln~(qe/(qe-q)=k_1t~(Eq.~4)) \end{array}$ 

For systems that satisfy this model, plotting ln ((qe-q)/qe) vs. t yields a straight line passing through the origin with a slope of k1. The conditions of the process determine the rate constant k1. It has been noted that it decreases when the initial bulk concentration rises [34,35], which may be translated as follows: The timescale for the process to reach equilibrium is  $1/k_1$ ; if the initial concentration  $(C_0)$  is higher, a longer period (smaller  $k_1$ ) is required. According to certain studies, k1 is either an increasing function of C<sub>0</sub> or independent of C<sub>0</sub> [36,37]. The experimental conditions, such as pH and temperature, will likely alter the k1 value. Because these two factors influence equilibrium behavior (isotherms), empirically isolating their impacts to the k1 value would be impossible. As expected, Small particle size correlates with big k1 values [38]. The validity of the PFO model for long adsorption has been argued when the system is close to equilibrium [39,40]. The model has also been demonstrated to be only valid at the beginning of the adsorption process [41]. The experimental settings and the amount of surface covered (adsorption time) influence the rate-controlling mechanism. As a result, a model's validity is restricted to a specific operating range of the supposed mechanism in which it was generated or interpreted [21].

A modified PFO equation is written as follows:  $dq/dt=k_1 qe/q (qe-q) (Eq. 5)$ 

The linearized form becomes:

 $q/qe+ln (qe-q) = ln (qe) -k_1t (Eq. 6)$ 

## Pseudo-Second-Order (PSO) Model

The pseudo-second-order kinetic equation has been frequently utilized in the study of adsorption kinetics to characterize the time development of adsorption in non-equilibrium situations [42]. The equation is as follows:  $dq/dt = k_2 (qe-q)^2 (Eq. 7)$ 

## Where:

 $k_2$ = pseudo-second-order (PSO) rate constant When equation (7) is integrated with the initial of

When equation (7) is integrated with the initial conditions of q =0 and t =0, the linearized form of the equation becomes:  $t/q = 1/k_2qe^2 + t/qe$  (Eq. 8)

The initial adsorption rate is  $k_2qe^2$ . For PSO-compliant kinetics, a t/q v s t plot yields a straight line. 1/qe is the slope, while 1/ $k_2qe^2$ is the intercept. Other linearized forms exist, though they are less commonly employed [43]. PSO can model most environmental kinetic adsorption well, suggesting its superiority over other models. The constant  $k_2$  is a time scale factor that decreases with rising C<sub>0</sub> like PFO does [44,45]. Because of the challenges that come from the impact on equilibrium isotherm shapes, the effects of pH and temperature on  $k_2$  have not been well investigated. Due to the lower IPD resistance, a smaller particle size results in a higher  $k_2$  value [38]. Based on pore diffusion and the Langmuir surface reaction, an adsorption–diffusion model was devised if the following conditions are met, their model gives an excellent fit to PSO kinetics: The conditions are as follows:

- (i) Reaction control, nonlinear (saturated) adsorption, and
- (ii) A sufficient amount of adsorbent to adsorb half of the adsorptive in the bulk phase. They claimed that, at least over a given time range, those PSO kinetics that could not be predicted by their model are governed by an unknown mechanism.

#### **Elovich Equation**

To describe the adsorption of carbon monoxide (CO) on manganese dioxide ( $Mn0_2$ ), Roginsky and Zeldovich proposed the term in 1934 [21]. The equation is expressed as:

dq/dt =  $\alpha \exp(-\beta q)$  (Eq. 9) When integrated, the equation becomes: q= 1/ $\beta$  ln (1+  $\alpha\beta$ t) (Eq. 10) The linearized form becomes: Q= 1/ $\beta$  ln ( $\alpha\beta$ ) + 1/ $\beta$  ln t (Eq. 11) A straight line should appear on the q vs. ln t plot if the Elovich equation is followed. The slope is 1/ $\beta$ , while the intercept is [ln ( $\alpha\beta$ )]/ $\beta$ . Where:  $\alpha$ = initial adsorption rate (mg/g)

 $\beta$  = desorption constant

The Elovich equation ignores desorption and is well-known for accurately describing chemisorption [46]. It's physically flawed since it predicts infinite q over large periods. As a result, it's appropriate for kinetics that are far from equilibrium, where desorption isn't possible due to a lack of surface coverage. Many attempts have been made to develop a theoretical foundation for the Elovich equation, with the majority of these publications assuming significant heterogeneity at the adsorbent surface [47]. This model has been used to simulate liquid-phase kinetics. The Elovich equation was found to be the best fit for lead adsorption onto activated carbon [48]. Dye adsorption on eggshell biocomposite beads was discovered to follow Elovich kinetics [49]. The constants  $\alpha$  and  $\beta$  rise with increasing initial dye concentration, as expected from their physical definitions. When the temperature of the bulk solution was raised, the observed values of  $\alpha$  increased, but  $\beta$  decreased [50].

## **Error Functions in Selecting Best Models**

Error functions are statistics that measure the discrepancy between model parameters and experimental results. The leastsquares criterion was used to build linear regression, which is a standard method [21]. The slope and intercept, which are both specified as functions of the experimental data, are good indicators of model parameters. The fitted parameters are determined via regression to reduce the sum-of-squares errors between the predicted and experimental values. The fitted parameters in standard nonlinear regression are also adjusted to minimize the sum-of-squares errors [51].

Rather than the most often used least squares function, other error functions might be defined as the objective function for data regression. Unlike linear regression, nonlinear regression is an interactive technique in which the values of model parameters are iterated based on a chosen algorithm to minimize the predetermined error function,  $R^2$  is to be maximized [43]. This regressive interaction can easily be achieved using computer software such as Matlab, OriginPro, Mathematica, and SPSS.

In the literature, these error statistics are calculated in addition to the correlation of determination ( $R^2$ ) to corroborate and support the model that R2 has already distinguished. In most circumstances, high R<sup>2</sup> values relate to low error statistics. RMSE is useful when the R<sup>2</sup> values are too close to distinguish between the PFO and PSO models [52]. El-Khaiary and Malash expressed worry about the possibility of bias when using R<sup>2</sup> as the goodness-of-fit criterion for models with varying degrees of freedom [53]. The following are some notable error functions:

- (a) Sum- of –Squares of Errors (SSE)
- (b) Chi-squared statistics (X<sup>2</sup>)
- (c) Mean sum of Squares Errors (MSE)
- (d) Root mean sum-of-squares Error (RMSE)
- (e) Normalized standard deviation (Dq%):
- (f) Average Relative Error (ARE
- (g) Coefficient of Determination/Correlation coefficient (R<sup>2</sup>)
- (h) Sum of absolute Error (SAE)
- (i) Marquadt's percent standard deviation (MPSD)

#### **Isotherm Studies**

Bacteria, fungi, and algae are all examples of microbial adsorbents, and their large surface area and variety of functional groups make them promising candidates for pollution removal from water solutions. Thorough isotherm and kinetic studies are necessary to comprehend the adsorption behavior of these microbial adsorbents. These studies aid in clarifying the processes at work and in optimizing the adsorption process for real-world applications. Isotherm investigations reveal the nature of the adsorption process and the capacity of the adsorbents at a constant temperature [54,55]. When analyzing adsorption data, many isotherm models are typically employed. Research on the isotherms and kinetics of various microbial adsorbents is included in **Table 3** below.

## Table 3. Isotherms and kinetic studies of some Microbial adsorbents.

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Microbial Adsorbent	Adsorbate (dye)	Isotherm	Kinetic	Adsorption capacity (mg/g)	Type of regression	Ref
Rhodopseudomonas sp. (Bacteria)	Astrazone red	Freundlich and	Not reported	Not reported	Non-linear	[56]
		Langmuir	1	1		
Aspergillus carbonarius and	Congo red	Langmuir	Pseudo-second- order	99.01 for Aspergillus carbonarius	Non-linear	[57]
Penicillium glabrum (fungi)				and 101.01 for Penicillium glabrum		
\Rhodococcus erythropolis	Crystal violet	Langmuir	Pseudo-second- order	289.8	Non-linear	[58]
(bacteria)		-				
Saccharomyces cerevisiae (fungi)	Astrazone blue	Langmuir		70	Non-linear	[59]
Phanerochaete chrysosporium	Remazol brilliant blue R	Langmuir	Pseudo second- order	101.06	Non-linear	[60]
(fungi)						
Penicillium restrictum (fungi)	Reactive black 5		Pseudo-second-order	98.33		[61]
Trichoderma harzianum (fungi)	Acid yellow 12	Freundlich	Pseudo second- order	78.39		[62]
Trichoderma harzianum (fungi)	Reactive black B	Freundlich	Pseudo second-order	97.42		[63]
Escherichia coli (bacteria)	Reactive Yellow 2			335.16		[[64]
Chlamydomonas variabilis		Freundlich and	Pseudo-second-order	115	Non-linear	[65]
(microalga)	Methylene blue	Langmuir				

Table 4. Some thermodynamic studies of triphenylmethane dyes adsorption.

Microbial biomass (adsorbent)	Adsorbate (dye)	Temperature (K)	$\Delta G$	ΔH (ki/mol)	∆S (j/mol)	Nature of adsorption	Ref
Cenhalasporium	Acid red -57	293	-22.38	-13.08	32.26	Spontaneous exothermic and there is an increase in the degree	[66]
aphidicola	Acid fed -57	303	-22.50	-15.00	52.20	of randomness at the solid-liquid interface during the adsorption	[00]
		313	-23.38			of fundomness at the solid inquid interface during the adsorption	
		373	23.30				
Panicillium rostrictum	Reactive orange	208	23.55	0.70	24.83	Non spontaneous endothermic and there is an increase in the	[67]
1 enternam restrictum	122	212	2.25	9.70	24.05	rendomness at the solid liquid interface during the adcomption	[0/]
	122	212	2.03			randomness at the solid-inquid interface during the adsorption	
		525	1.39				
Aspergillus foetidus	Reactive black-5	303	-12.2	12.2	80.4	Spontaneous, endothermic and there is an increase in the	[68]
		323				randomness at the solid-liquid interface during the adsorption	
Bacillus macerans	Basic blue- 41	298	-4.72	-22.90	-0.061	Spontaneous, exothermic, and decrease in the degree of	[69]]
		308	-3.91			randomness at the solid-liquid interface during the adsorption	
		318	-3.25			1 0 1	
		328	-2.09				
Paonihacillus macarans	Acid blue 225	208	25.62	107 72	273 62	Spontaneous exothermic and decrease in the degree of	[70]]
1 denibacilius macerans	Acid blue 225	298	24.81	-107.72	-275.02	randomness at the solid liquid interface during the adsorption	[/0]]
		210	-24.01			randomness at the sond-inquid interface during the adsorption	
		328	-12.79				
Trichoderma harzianum	Acid blue 062	298	-25.87	-50.07	-81.50	Spontaneous, exothermic, and decrease in the degree of	[63]
(fungi)		308	-25.43			randomness at the solid-liquid interface during the adsorption	
		318	-23.50				
		328	-21.87				
	Acid yellow 12						
		298	-5.51	26.90	108.5		
		303	-6.05				
		310	-6.81				
		313	-7.14				
Stuantonnoor funding	Mathulana hlua	208	5254 2/	1 25 04	100.07	Spontaneous exothermic and decreases in the decreas of	[71]]
(hostoria)	Wieuryiene blue	290	-5554.24	-55.04	-100.07	rendemness in the adsorption	[/1]]
(bacteria)		212	2722.04	,		randomness in the adsorption	
		515	-3723.03	7			
	Congo red		-2320.17	·			
	8	298	-1996.15	5 -17.47	-50.94		
		303	-1491.06	5			
		313		·			
Aspergillus	Congo red	293	-3.05	48.42	154	Spontaneous, endothermic, and increase in the degree of	[72]
carbonarius (fungi)	8	298	-2.61			randomness of the adsorption	r1
g-)		303	-1 50				
Penicillium glahrum		293	-2.99	74 3	243		
(fungi)		298	-1 31	, 115	2.0		
(lungi)		270	-0.57				
Rhodococcus	Crystal violet	298	-26.13	-13.08	40	Spontaneous, exothermic, and increase in the degree of	[58]
erythropolis (bacteria)		308	-26.98			adsorption randomness	
		318	-27.25				
		328	-27.50				
Trichoderma harzianum	Reactive black B	298	-2.750	-42.53	151	Spontaneous, exothermic, and increase in the degree of adsorption randomness	[62]]
(fungi)		303	-3.478				
( 67)		308	-4.499			-	
		313	-5.551				
Savaassum hominhull	Mathulana hlua	202	3 5 2	7 16	37 15	Spontaneous evolution and increases in the degree of	[72]
(macroalga)	wiedrytene ofde	295	-3.55	7.70	57.75	randomness	[15]
(		313	-429			ianaonino oo	
		515	741				

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#### **Thermodynamic Studies of Microbial Adsorbents**

To fully grasp the spontaneity, nature, and practicability of adsorption processes utilizing microbial adsorbents, thermodynamic studies are important. These investigations shed light on the energy changes that occur during adsorption, which in turn helps to explain how microbial biomass can remove toxins from water and what kinds of uses it could have. The driving forces behind adsorption processes are described by important thermodynamic parameters, which include the changes in Gibbs free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ), and entropy ( $\Delta S$ ). **Table 4** below displays the results of several thermodynamic investigations on the adsorption of triphenylmethane dyes.

## CONCLUSION AND FUTURE WORKS

As a characteristic of both living and nonliving biomass and associated products, biosorption is undeniably an important environmental process and an integral part of many conventional waste treatment approaches. This method shows promise for the removal of heavy metals, dyes, and other harmful compounds from wastewater by the passive binding of contaminants from aqueous solutions by biological organisms. Despite its promise, biosorption has only found limited application in industry thus far, especially when used in conjunction with more conventional methods of pollutant treatment in hybrid systems. The lack of widespread industrial use is mostly attributable to three factors: the necessity for improved biosorbents, a deeper knowledge of biosorption mechanisms, and thorough economic evaluations.

In the future, research ought to center on finding and creating novel biosorbents that are more efficient and selective for particular pollutants. Because of their abundant functional groups and large surface areas, microbial biomass—which includes bacteria, fungus, and algae—has the potential to bind contaminants. These organisms could be genetically engineered to have better biosorptive capabilities, allowing them to target and remove toxins more effectively. Agricultural and industrial waste products have the potential to be inexpensive biosorbents, which could lead to sustainable and cost-effective solutions for large-scale applications. In order to forecast how biosorbents would operate in different environments, more accurate biosorption models are required. If these models are to give a full picture of biosorption, they need to include things like temperature, ionic strength, pH, and competing ions.

It is possible to optimize the biosorption process by using advanced modeling approaches, such as machine learning and artificial intelligence, to examine complicated datasets. This would improve the biosorption systems' design and make them more useful in industrial settings. To make biosorbents work better, we need a better understanding of the molecular mechanisms that drive biosorption. The precise ion exchange, complexation, and physical adsorption interactions between biosorbents and pollutants should be the subject of future research. Scientists use molecular modeling, spectroscopy, and microscopy to better understand these processes. Biosorbents can be improved to remove pollutants more effectively by modifying them according to the knowledge gathered from these investigations, which increases their binding capacity and selectivity.

To promote biosorption technology adoption in industry, thorough evaluations of its commercial viability and financial feasibility are required. Considering variables including raw material costs, operational expenditures, and possible revenue from the recovery of valuable byproducts, future study should evaluate biosorption's cost-effectiveness compared to current treatment approaches. Research into the market should pinpoint promising sectors and geographic areas for biosorption and any obstacles to its widespread use. Tackling these problems and promoting the wider application of biosorption technology would require close collaboration between researchers, industry partners, and politicians. In order to make biosorption more useful in the real world, researchers should look into ways to combine it with other wastewater treatment methods in the future.

Synergistic effects, increased treatment efficiency, and decreased costs could result from hybrid systems that integrate biosorption with other processes, including coagulation, flocculation, and membrane filtering. Validating the performance and scalability of these hybrid systems will require studies conducted on a smaller scale as well as real-world demonstrations. For biosorption technologies to be used safely and sustainably, evaluating their effects on human health and the environment is crucial. The post-treatment destiny of pollutants and the hazards connected with disposing of used biosorbents should be the subjects of future studies. The development of ecofriendly techniques can be guided by life cycle assessments, which offer a comprehensive view of the environmental impact of biosorption processes. If these areas of future study are adequately funded, biosorption could replace more traditional methods of pollution removal as the industry standard, providing a low-cost, low-impact answer to some of the world's most critical environmental problems.

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