Biosorption of Bromo-based Dyes from Wastewater Using Low-Cost Adsorbents: A Review

Ebenezer Olujimi Dada[1], Ilesanmi Ademola Ojo[1,2],
Abass Olanrewaju Alade[1,2,3*], Tinuade Jolaade Afolabi[1,2],
Monsurat Omolola Jimoh[1] and Monsuru Olatunji Dauda[1,2]

[1]*Department of Chemical Engineering, Ladoke Akintola University of Technology Ogbomoso (LAUTECH), Nigeria.*
[2]*Bioenvironmental, Water and Engineering Research Group (BWERG), Ladoke Akintola University of Technology Ogbomoso, Nigeria.*
[3]*Science and Engineering Research Group (SEARG), Ladoke Akintola University of Technology Ogbomoso, Nigeria.*

Authors' contributions

This work was carried out in collaboration among all authors. Authors EOD and AOA designed the study. Author IAO wrote the first draft of the manuscript. Author TJA managed the analyses of the study. Authors MOJ and MOD managed the literature searches. All authors read and approved the final manuscript.

Review Article

ABSTRACT

The dyes in the effluents discharged into water bodies, aimlessly, are displeasing aesthetically and pose hazards to aquatic communities. The use of adsorption process has been adopted for effective treatment of wastewater containing dyes. The removal of Bromophenol blue (BPB), Bromocresol green (BCG), Bromocresol purple (BCP), and Bromothymol blue (BTB) dyes (a family of triarylmethane dyes) through adsorption process using several cheaply available non-conventional agricultural-waste based adsorbents was reviewed in this report. The gaps in the treatment trend further indicate the prospect of adapting various lignocellulose and other biogenic materials for the removal of Bromo-based dyes from wastewater.

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Corresponding author: E-mail: aoalade@lautech.edu.ng;

1. INTRODUCTION

The contamination of natural waters has become one of the greatest problems confronting the ecosystem in Nigeria. Effluents released from various dye-using industries are harmful to the ecosystem, and subsequently, the need to remove dye from the water [1]. The textile industry contributes about 22% of the total volume of industrial wastewater generated in Nigeria [2]. The release of dyes and other pollutants into water bodies by industries is undesirable and poses serious environmental challenges to the entire ecosystem. This is due to the toxic, mutagenic, and carcinogenic nature of dyes [3]. Coloured wastewater discharged into streams reduces light penetration hence photosynthetic activity is inhibited [4].

The development of a cost-effective and environmentally safe mechanism to remove the dye and other contaminants has been a challenging exercise for the general populace. With the increasingly stringent laws on the industrial discharge of wastewater, it has become imperative to treat wastewater [5]. Biosorption method is considered as a very effective as well as an efficient method of treating industrial waste effluents. It offers significant advantages such as low-cost, availability, profitability, easy operation, and high efficiency [6].

Several techniques (adsorption, Ion exchange, Membrane filtration, and others) are currently being used for pollutants removal from wastewater containing dyes and other contaminants. However, an environmentally friendly method, the biosorption process has proved to be very efficient at removing dyes from effluents [7]. Activated carbon, because of its large surface area, microporous structure and high adsorption capacity is currently the most widely used adsorbent [8]. However, due to the high cost, its usage has been limited in the large-scale treatment of wastewater. Therefore, efforts are on the rise to improve on the existing mechanisms to increase the efficiency of the process. This entails researching into the use of agricultural wastes (biomass) for the preparation of adsorbents (biosorbent) especially for the removal of dyes, as well as other pollutants in the wastewater. The agricultural wastes that have been investigated among others include *Posidonia oceanica (L.) fibre* [9], Orange and Banana Peels [10], Peanut Hull [11], Pumpkin Seed Hull [12], *Citrullus lanatus* Rind [13], Broad Bean Peel [14], Oil Palm Fiber: Activated Carbon [14], Oil Palm Trunk Fiber [14], Almond Shell [15], Leaf Powder [16], Rice Husk [17], Sawdust [17], Garlic Peel [18], Pine Apple Stem [19], Rice Bran and Wheat Bran [20], Papaya Seeds [21] and Sugarcane Bagasse Fly Ash [22]. Chicken feathers [23], Pomelo Citrus Grandis Peel [24] and groundnut shell [25] are biosorbents used for the removal of other contaminants in wastewater.

In the present review, an attempt has been made to enumerate in general, how biosorption has been utilized in the removal of dyes and other contaminants from wastewater, and specifically how various biosorbents have been utilized in the removal of Bromophenol blue (BPB), Bromocresol green (BCG), Bromocresol purple (BCP), and Bromothymol blue (BTB). The future of biosorption with respect to how productivity and efficiency can be increased with the advances in modern technology is also discussed.

2. DYES

A dye is a coloured material applied on a substrate using either dyeing, printing, surface coating process, and so on. The production and application of dyes constitute one of the oldest arts in nature. Dyes can be described as water-soluble and water-dispersible organic compounds with the ability to be adsorbed into the substrate while distorting and disrupting the crystal structure of the substrate [26]. Dyes can be categorised as anionic (direct, acid, and reactive dyes), cationic (basic dyes) and non-ionic (disperse dyes) [27,28].

2.1 Challenges of Dye in the Environment

An effluent (dye-containing wastewater) from textile industries is considered as one of the most harmful effluents with adverse effects on the ecosystem. Report from various previous works pointed out that some classes of dye, especially azo dyes and their derivatives, may be carcinogenic and/or mutagenic [29]. It is almost impossible to remove these classes of dyes from the environment because of the highly stable nature of their compounds.

2.2 Triarylmethane Dyes

Triarylmethane dyes are chemical (organic) compounds that are formed from

triphenylmethane. BPB, BCP. BCG and BTB are examples of triarylmethane dyes with hydroxyl groups at the *para* positions of at least two aryl groups. As dyes, these compounds have intense colours.

BPB is used as a pH indicator, a colour marker, and a dye. It is an acid-base indicator whose useful range lies between pH 3.0 and 4.6. It changes from yellow at pH 3.0 to blue at pH 4.6. BPB has a characteristic green-red colour [30]. The chemical formula is $C_{19}H_{10}Br_4O_5S$ and has a molar mass of 669.96 $gmol^{-1}$. It has a melting point of 273°C (523°F; 546 K), the boiling point of 279°C, and stable for two years at room temperature. It has a maximum wavelength of 206, 283 and 424 nm; a typical structure of BPB is shown in Fig. 1a. [31].

BCG is also used as a pH indicator as well as a growth medium for microorganisms. The most common use of BCG is for measuring serum albumin concentration within mammalian blood samples in possible cases of kidney failure and liver disease [32]. In aqueous solution, BCG will ionize to give the monoanionic form (yellow), that further deprotonates at higher pH to give the di-anionic form (blue), which is stabilized by resonance. The structure of BCG is shown in Fig. 1b.

BCP or 5′, 5″-dibromo-*o*-cresolsulfophthalein, is a pH indicator that exhibits colour yellow below pH 5.2, and violet above pH 6.8. In microbiology, it is used for staining dead cells based on their acidity, and for the isolation and assaying of lactic acid bacteria. The structure of BCP changes with pH and results in a shift in the equilibrium between two different structures that have different colours (Fig. 1c). In near-neutral or alkaline solution, the chemical has a sulfonate structure that gives the solution a purple colour. As the pH decreases, it converts to a sultone (cyclic sulfonic ester) that imparts a yellow colouration to the solution [33].

BTB is mostly utilised in applications where neutral pH is required. It is often used to detect and calibrate the presence of carbonic acid in a liquid. The peak absorption of a protonated form of BTB is at 427 nm, this indicates it can transmit yellow light in acidic solutions, and the deprotonated form has its peak absorption at 602 nm which indicates the transmission of blue light

in more basic solutions. Highly acidic BTB is magenta in colour [34]. The presence of one moderate electron-withdrawing group (bromine atom) and two moderate donating groups (alkyl substituents, as shown in Fig. 1d) are responsible for BTB's active indication range from a pH of 6.0-7.6. BTB is slightly soluble in oil but soluble in water, ether, and aqueous solutions of alkalis. It is less soluble in nonpolar solvents such as benzene, toluene, and xylene, and certainly not soluble in petroleum ether [35]. BTB has been used for observing photosynthetic activities, or as a respiratory indicator (turns yellow as CO_2 is added). BTB is used in obstetrics for detecting premature rupture of membranes [35].

2.3 Current Treatment Technologies for Dye Removal

Dyes are chemically stable, hence difficult to biodegrade [37]. The methods reported treating effluents that contain dyes are discussed under the following subheadings.

2.3.1 Biological treatments

Biological treatment, which is one of the most commonly used techniques in the treatment of dye-containing wastewater can be aerobic, anaerobic or a combination of both. The aerobic process involves the breaking down of the organic compounds (dyes) in the wastewater by the enzymes secreted by bacteria present in the wastewater [38]. The process is relatively inexpensive, as well as having low running costs [39]. However, total removal or degradation of pollutants may not be possible as some of these organic compounds (dyes) of synthetic nature have a very complex chemical structure that is not easily broken down or degraded [40]. Other factors responsible for this ineffective colour degradation are high concentration of pollutants, dyestuff concentration, initial pH and temperature of the effluent. The main drawbacks of the biological treatment are low biodegradability of the dyes, less flexibility in design and operation, larger land area requirement and longer times required for decolourisation – fermentation processes, thereby making it incapable of removing dyes from effluent continuously in liquid state fermentations. All these contribute to not making this process efficient in wastewater treatment.
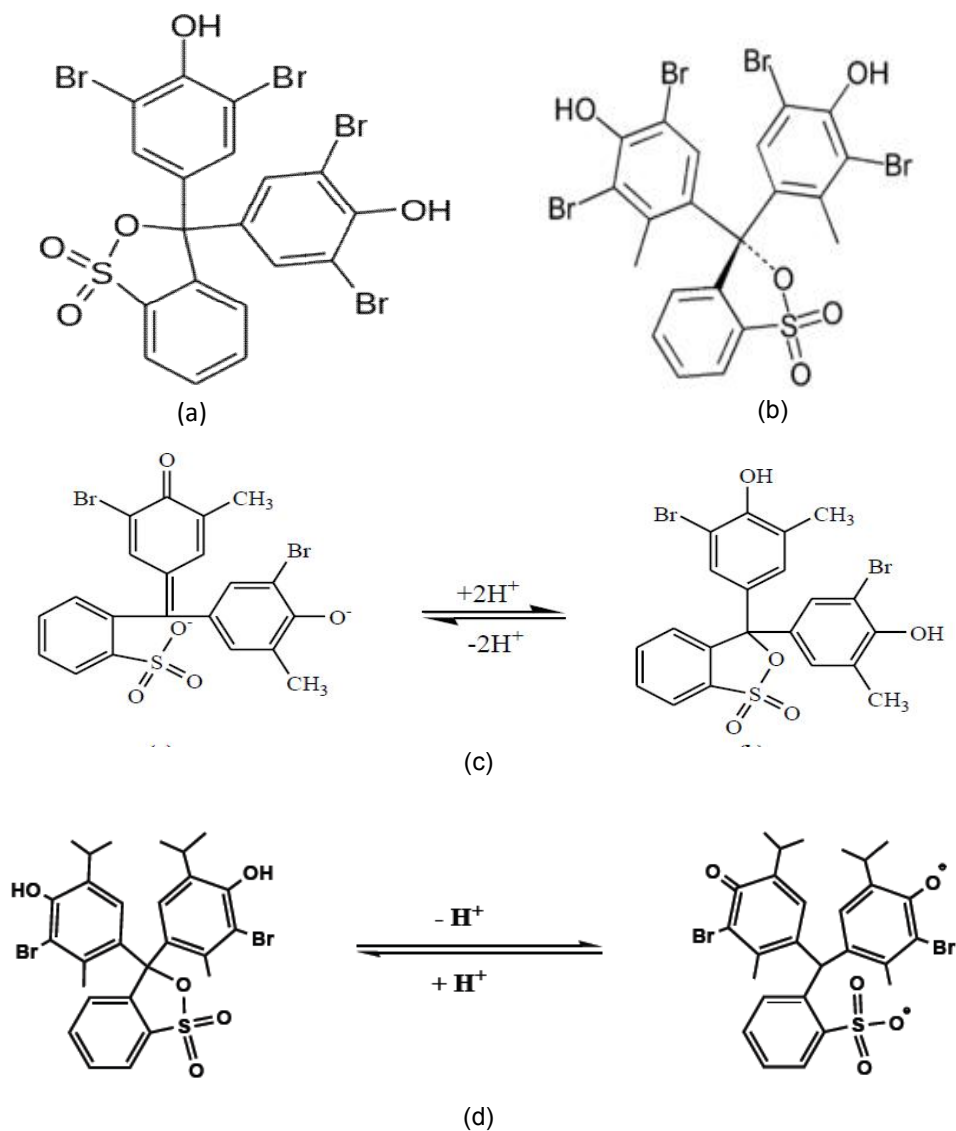
Fig. 1a. Structure of bromophenol blue [31], 1b: Structure of bromocresol green [36], 1c: Structure of bromocresol purple [33] and 1d: Structure of the acidic and basic forms of bromothymol blue [35]

2.3.2 Chemical treatments

Chemical treatments include coagulation or flocculation, combined precipitation flocculation with Fe(II)/Ca(OH)$_2$, electro flotation, electrocoagulation, irradiation and advanced oxidative process [41,42]. In these types of treatments, there is the possibility of formation of intermediate product which constitutes a secondary pollution problem leading to excessive chemical use. Although these methods have proven to be very effective for the treatment of water contaminated with pollutants, they are highly exorbitant and commercially cumbersome.

High electrical energy demand and consumption of chemical reagents are common problems associated with this type of treatment [43]. In most cases, the final products from these processes are concentrated sludge produced in large quantities, this further compounds pollution phenomenon [44].

2.3.3 Physical treatments

Physical treatments include membrane-filtration processes and adsorption techniques. Filtration technologies include microfiltration, ultrafiltration, nanofiltration, and reverse osmosis.

Microfiltration is rarely used for wastewater treatment due to its large pore size [45]. The main disadvantages of this method are high working pressures, vast energy consumption, high-cost spare-parts i.e. membrane and a relatively short membrane life, these disadvantages inhibit efficient delivery of service for this method for removal of pollutants from wastewater [46]. Reverse osmosis is an effective decolouring and desalting process against the most diverse range of dye wastes and has successfully been employed for recycling, however, it is very costly [47].

2.3.4 Advanced oxidation process (AOP)

The advanced oxidation process is designed to remove organic and some inorganic materials in wastewater by oxidation through reactions with hydroxyl radicals (OH). However, the relatively high capital, operating and maintenance costs of this sophisticated process are some of its disadvantages [42].

2.4 Methods of Dye Removal

There is no single standard methodology/ treatment procedure used for all types of wastes. However, some of the major techniques used for wastewater treatment are enumerated in Table 1 [48,49].

2.5 Agricultural Waste Materials Used as Low-Cost Adsorbents-Biosorbents

Biological materials used to accumulate and concentrate dyes from aqueous solution are termed as bio adsorbents. Some of the proven efficient adsorbent materials are peanut hull, orange and banana peels, pumpkin seed hull and *Posidonia oceanica (L.)* fibre [50]. The major disadvantage in these biomaterials is its non-selective to target and non-target contaminants. Unlike the conventional ion exchange, the process is selective to the ions it needs to adsorb. Bio adsorption is a novel approach and is considered to be relatively superior to other techniques because of its low cost, simplicity of design, high efficiency, and ability to separate wide dyes [50].

The use of the various microbial, plant and animal biomass as biosorbent has received substantial attention from various researchers, due to the wide availability of biomass materials, cost-effectiveness and cheap availability of the biosorbents. This phenomenon is set to provide new opportunities for pollution control, element recovery and recycling process [50]. Some biomasses come as waste material from fermentation industries or as renewables. In either case, the costs of biomass raw materials are extremely low. The use of microorganisms as biosorbents for dyes also offers a potential alternative to other adsorbents [51]. The cell wall of microorganisms, which consists essentially of various organic compounds such as chitin, lipids, amino acids and other cellular components, can provide a means for the passive uptake of dyes [52].

Various forms of biomass such as macroalgae (seaweeds), plant materials (leaves, bark and sawdust), animal materials (hair, crustaceans) have also been studied. All were regarded as wastes that could be converted into a useful commodity for the production of biosorbents [53]. Availability is a major factor to be considered in selecting the biomass to be used [54]. Biomasses that come from industrial wastes already have various microorganisms in large amounts naturally, with such organisms being well suited for quick cultivation or propagation biosorption purposes [55].

Seaweeds are naturally conditioned for biosorption because their macroscopic structures offer a suitable basis for the production of biosorbent particles suitable for sorption process applications. Some chemical components of yeast cells may be used as ion exchangers with the rapidly reversible binding of cations. The strong biosorbent characteristic of some types of microbial biomass with respect to dyes depends on the function of the chemical composition of such microbial cells. The biomass may be dead while all cells are metabolically inactive [55].

2.6 Other Adsorbents

2.6.1 Activated Carbon (AC)

Activated Carbon (AC) is a black, amorphous solid containing a major portion of fixed carbon content and other materials such as ash, water vapour and volatile matters in a smaller percentage. These components have been subjected to chemical processes aimed at increasing its porosity. Activated carbon is one the best effective sorbents used in removing dyes and heavy metals from a wide range of industrial wastewater, contaminated groundwater and landfill leachate [56]. Dyes adsorption onto activated carbon is greatly influenced by the

chemical and physical properties of the activated carbon [57]. AC is available in different forms such as powdered, granulated, fibrous, spherical, and cloth forms. Powdered activated carbon has a very fine particle size of about 44μm, which enhances faster adsorption. The granulated activated carbon has granules of 0.6 to 4.0mm in size. Fibrous activated carbon fibre has a large surface area and contains a higher percentage of larger pores [58,59,60].

2.6.2 Siliceous materials

Silica-based adsorbents cover a wide range of applications. The choice of these materials for use is due to its high porosity, large inner surface area, and the high adsorption properties of the available materials [61].

2.6.3 Natural zeolites

Natural zeolites are environmentally and economically friendly hydrated alumina silicate materials with excellent ion exchange and sorption properties. Zeolites are cheap, exhibit excellent selectivity for different cations at low temperatures, compact in size and allow simple and cheap maintenance in the full-scale applications [62].

2.6.4 Clay

Clay is a naturally occurring material which is made up of fine-grained minerals, which might be plastic in nature at appropriate water contents and thereafter hardens when dried or burnt [63]. Bentonite is the most common and effective type of clay used for water treatment. It is a clay mineral consisting mostly of montmorillonite. Other clay minerals found in it are beidellite, kaolinite, saponite, hectorite and nontronite [63].

2.7 The Removal of BPB, BCG, BCP and BTB from Wastewater

The excellent ability and economic promise of adsorbents prepared from biomass and waste materials that exhibited high sorption properties for the removal of BPB, BCG, BCP and BTB from wastewater, in comparison with other adsorbents are summarized in Tables 2-5. This review has made a tremendous effort to highlight the maximum adsorption capacities isotherm, kinetic, thermodynamic data including optimal adsorption parameters of agricultural waste, industrial solid waste and nanoparticle-loaded based activated carbons for the removal of BPB (Table 2).

2.7.1 Activated charcoal

Adsorption of dyes from aqueous media on activated charcoal was carried out by Iqbal & Ashiq [64]. It was observed from the work that adsorption of all the dyes on activated charcoal is inversely proportional to the pH and temperature. The adsorptive removal of BCG from aqueous solution using activated carbon prepared from rice husk was investigated by Onu et al. [65]. The result indicated that an increase in contact time, adsorbent dosage and temperature increased the percent uptake of the BCG dye. Maximum percentage adsorption of about 93% was obtained. Langmuir isotherm models best described the equilibrium data of the adsorption process. Pseudo-second-order kinetic model best correlates the kinetics of the experimental data. The work showed that activated carbon prepared from rice husk can be used in adsorptive removal of BCG dye from solution and that the adsorption process was spontaneous and exothermic.

2.7.2 Mesoporous MgO nanoparticles

The removal of BPB dye using mesoporous MgO nanoparticles was investigated by Ahmed & Abou-Gamr, [66]. The results of the work showed that adsorption equilibrium data fitted well to the Langmuir and Freundlich isotherms. The adsorption isotherms indicated that the adsorption capacity is 40 mg.g^{-1} for BPB. The adsorption process follows the pseudo-second-order rate equation. The enthalpy change for BPB dye was 7.3kJ mol^{-1}. The process is endothermic and spontaneous. The work shows the ability of MgO Nanorods as an efficient and excellent adsorbent for the removal of two anionic dyes due to the higher point of zero charge of MgO [66].

2.7.3 Sorel's cement nanoparticles

Sorel's cement nanoparticles prepared via sol-gel method was used for the removal of BPB from their aqueous solutions by Ahmed et al. [67]. The effects of contact time, adsorbent dosage, initial dye concentration and temperature on removal efficiency were investigated. Adsorption data showed better fitting to the Freundlich isotherm equation. Langmuir model represented the results with lower but acceptable correlation coefficients implying surface heterogeneity. The maximum adsorption was 4.88 mg/g. The adsorption of BPB followed the pseudo-first-order kinetics.

Removal of the dye proceeded endothermic with ΔH of 7.8 kJ/mol. Obtained results indicate that Sorel's cement represents an efficient adsorbent for removal of BPB from aqueous solution.

2.7.4 α -chitin nanoparticles

The adsorption of BPB by α-chitin nanoparticles (CNP) using unique nanoparticles of 650 nm was studied by Rameshthangam et al. [68]. The results showed that the adsorption process increased with increase in the concentration of CNP, contact time and temperature. The adsorption process decreased with an increase in the initial dye concentration. It obeys Langmuir isotherm and pseudo-second-order kinetics more effectively. The isotherm and kinetic models confirmed that CNP could be used as a suitable adsorbent material for the removal of dyestuff from effluents.

2.7.5 Magnetic Fe_3O_4/MIL-88A nanocomposite

Huajiao et al. [69] stated in a study that Metal-organic frameworks are considered as good materials for the adsorption of many environmental pollutants. The results of the study showed that the magnetic Fe_3O_4/MIL-88A composite maintained a hexagonal rod-like structure and has good magnetic responsibility for separation. The maximum saturation magnetization was 49.8 $emug^{-1}$. The maximum adsorption capacity of Fe_3O_4/MIL-88A composite for BPB was 167.2 mg/g and could maintain 94% of the initial adsorption amount after five cycles. The pseudo-second-order kinetics and Langmuir isotherm models mostly fitted to the adsorption

for BPB suggesting that chemisorption is the rate-limiting step for this monomolecular-layer adsorption.

Ghosh & Biswas, [70] investigated the use of Labeo beta fish scale as an adsorbent for BPB removal. The scales showed good BPB removal performance at *p*H 4.8. The kinetic data acquired at that *p*H fits well both with the pseudo-second-order and the Weber-Morris kinetic equations. The data of adsorption equilibriums were best described by the Freundlich model. Thermodynamics shows that the BPB adsorption by the fish scale is spontaneous (ΔG^0 = negative, ΔH^0 = -21.49 kJ. mol^{-1} and ΔS^0 = + 27.75 $J.mol^{-1}.K^{-1}$). The BPB adsorption by the tested fish scale has taken place with the electrostatic mechanism.

2.7.6 Raw maize cob

Abubakar & Ibrahim, [31] studied the adsorption of BPB onto raw maize cob from aqueous solution. Results showed that BPB percentage was 96.53%, with equilibrium time within 125 minutes. The removal efficiency was found to increase with increasing initial dye concentration from 10 mg/l to 100 mg/l be high at lower pH. Also, an increase in the dosage of the adsorbent leads to an increase in the adsorption capacity for BPB. The adsorption process was found to fit closely to the Pseudo second-order model. The adsorption was feasible and spontaneous. The result indicated that raw maize cob could be used as an adsorbent for the removal of the tested dyes.

Table 1. Methods for dyes removal [48,49]

Processes	Method	Advantages	Disadvantages
Fenton reagents	Oxidation reaction using mainly $H_2O_2Fe(II)$	Effective decolourization of dyes	Sludge generation
Ozonation	Oxidation reaction using ozone gas	Gaseous state: no alteration of volume	Short half-life
Photochemical	Oxidation reaction using H_2O-UV	No sludge generation	Formation of by-products
NaCl	Oxidation reaction using Cl^+ to attack the amino group	Initial and acceleration of azo bond cleavage	Release of aromatic amines
Electrochemical destruction	Oxidation reaction using electricity	Non-hazardous compounds	The high cost of electricity
Activated carbon	Dye removal by adsorption	Good removal of a wide variety of dyes	Regeneration difficulties
Membrane filtration	Physical separation	Removal of all dye types	Production of sludge
Ion exchange	Ion exchange resin	Regeneration: no adsorbent loss	Not effective for all dyes
Electrokinetic coagulation	Addition of ferrous sulphate and ferric chloride	Economically feasible	High sludge production

Table 2. Maximum adsorption capacities of agricultural, industrial solid and nanoparticle-loaded based activated carbons for BPB

S/N	Adsorption	Adsorption capacity, q_{max} (mg/g)	Isotherm study	Kinetic study	Thermodynamic study	pH	Initial dye Conc. (mg/l)	Equilibrium time (min)	Dosage of Adsorbent (g/L)	References
1	Certain Fungi (Dried biomasses)	526	Langmuir	PSO	-	2.0	800	5hrs	1.0	[71]
2	Rhizopus Stolonifer Biomass	1111	Langmuir	PSO	Exothermic	2.0	600			[72]
3	Activated charcoal	9.0×10^{-3}	Langmuir		Exothermic	5.0	6.7 ppm	30	0.01	[64]
4	Fungus Aspergillus Flavus				Exothermic					[73]
5	Mild Steel in Acidic Medium	-3.58	Langmuir		Exothermic			7 days		[74]
6	ZnO assisted photocatalysis		Langmuir	PFO	-	8.0	600	30	0.6	[75]
7	Supported ionic liquids	47.5	Langmuir	PSO	endothermic	7.0	50	30	1.0	[76]
8	Sorel's cement nanoparticles	4.88	Freundlich	PFO	endothermic	8.3	25.14	90	0.2	[67]
9	a-chitin nanoparticles	22.72	Langmuir	PSO	endothermic	6.0	15	15	2.0	[68]
10	Gelidium Cartilagineum Powder	11.8991	Langmuir	PFO	endothermic	5.0	20	24	0.25	[30]
11	Silica-based aerogels	1029	Langmuir	PSO			44.0	120		[77]
12	Mesoporous MgO nanoparticles	40	Langmuir and Freundlich	PSO	endothermic	8.3	28	90	0,1	[66]
13	Acid Activated Clay	14.493	Langmuir	PSO	Exothermic	2.0	100	60	1.0	[78]
14	Raw Maize Cob	0.318	Temkin	PSO	Exothermic		100	125	1.5	[31]
15	Magnetic Chitosan-Graphene Oxide Composite	9.5	Langmuir		Endothermic	5.0		60	0.1	[79]
16	Magnetic Fe_3O_4/MIL-88A Nanocomposite	167.2	Langmuir	PSO			300	60	0.1	[69]

S/N	Adsorption	Adsorption capacity, q_{max} (mg/g)	Isotherm study	Kinetic study	Thermodynamic study	pH	Initial dye Conc. (mg/l)	Equilibrium time (min)	Dosage of Adsorbent (g/L)	References
17	Labeo beta Fish Scale	7.39	Freundlich	PSO	Exothermic	4.8	16.0	45	4.0	[70]
18	Modified exuviae of Hermetia illucens larvae	571	Langmuir	PFO	Exothermic	4.0	200	20	0.2	[80]

Key: PFO – Pseudo first order
PSO – Pseudo second order

Laboratory investigations of the potential use of dried biomasses of *Rhizopus stolonifer, Fusarium sp., Geotrichum sp., and Aspergillus fumigatus* as biosorbents for the removal of bromophenol blue dye from aqueous solutions were conducted by Kang et al. [71]. Kinetics studies indicated that the BPB dye uptake processes could be well described by the pseudo-second-order model. The fungal biomasses exhibited the highest dye biosorption at pH 2.0. The Langmuir adsorption model appears to fit the dye biosorption better than the Freundlich model, with maximum dye uptake capacities ranging from 526 to 1111 mg/g, depending on the biomass used.

2.7.7 *Rhizopus stolonifer* biomass

The removal of BPB dye, from aqueous solutions, by biosorption on non-living biomass of *Rhizopus stolonifer* was investigated in a batch system by Kim et al. [72]. Pre-treatment of the biomass with NaOH was found to be the most effective means to enhance the biosorption of BPB. The fungal biomass exhibited the highest dye sorption capacity at pH 2 and the uptake process followed the pseudo-second-order model. The adsorption capacity of the biomass increased as the initial dye concentration increased, and the maximum uptake value was estimated at 1111 mg/g according to Langmuir adsorption isotherm. The high efficiency of biosorption and elution, low biomass damage, and stability of over prolonged operation time make the process an economical effective alternative technique for dye pollution monitoring.

2.7.8 Modified exuviae of *Hermetia illucens larvae*

Pablo et al. [80] developed biosorbent from the exuviae of *Hermetia illucens (Linnaeus) larvae* and used it to remove organic anionic dyes from an aqueous medium. The maximum adsorbed amount was 571 mg g^{-1} according to Langmuir's model. The adsorption process was evaluated as exothermic and spontaneous. The process was classified as physical adsorption. The prepared biosorbent was tested in five consecutive adsorption cycles achieving 99% dye removal at each stage. These results suggest that the prepared biosorbent had potential applications in the treatment of effluents from textile industries.

2.7.9 UV- Radiation with ZnO as Catalyst

The adsorption of BPB dye solution on the metal oxide semiconductors studied by Mashkour, [75]

was found favourable by the Langmuir approach. The photocatalytic decolourization follows pseudo-first-order kinetics at low initial dye concentration. The initial decolourization rates could be fitted to the empirical Langmuir-Hinshelwood equation up to 15 mg/L, i.e. the decolourization rate of the BPB dye solution. According to the Langmuir-Hinshelwood kinetic model, it is concluded that ZnO acts as a better photocatalyst to degrade the BPB dye solution under the optimum physicochemical conditions.

2.7.10 Mild steel in acidic medium

The compounds BPB studied as inhibitors slowed the acid corrosion of steel to some extent being physically adsorbed on the metal surface [74]. The inhibition efficiency increases with increase in inhibitor concentration and decreases with increase in temperature. The values of q_{ads} obtained at 303K and 313K are all negative indicating that the inhibitors are strongly adsorbed on the steel surface and the adsorption process is spontaneous. Inhibition of steel corrosion by BPB obeyed Langmuir adsorption isotherm. The synergistic effect between BPB and KBr can be explained by the fact that the addition of the KBr component stabilized the adsorption of the inhibitor dyes on the steel surface. This stabilization may be caused by the interaction between the dyes and Br$^-$ ions. Thus, the interaction enhances the inhibition efficiency to a considerable extent due to the increase of the surface coverage in the presence of bromide ions.

2.7.11 *Gelidium cartilagineum* powder

Raju & Satyanandam, [30] reported in an extensive study of adsorption of *Gelidium cartilagineum* powder unto BPB dye that the equilibrium agitation time for BPB biosorption was 25 minutes. The percentage biosorption of BPB dye decreased with increase in biosorbent size from 53 µm (56%) to 152µm (38%). Percentage biosorption of BPB dye from the aqueous solution increases significantly with an increase from pH2 (53%) to pH6 (74%). The optimum biosorption dosage was 25 g/L. The maximum uptake capacity of 11.8991 mg/g was obtained at 308 K. Entire total system followed Langmuir Isotherm and Langergren First order Kinetics. Thermodynamics revealed that the system is endothermic, spontaneous and irreversible. *Gelidium cartilagineum* powder is an effective and efficient biosorbent and is capable of removing BPB dye.

2.7.12 Novel supported ionic liquids

New adsorption materials, supported ionic liquids, have been successfully applied for dyes separation by Hang et al. [76]. Studies showed that the kinetic data were well described by the pseudo-second-order kinetic model. Moreover, the isotherm experiments revealed that the Langmuir model yielded better fitting than the Freundlich model for BPB adsorption. The calculated thermodynamic parameters indicated that the adsorption of BPB was spontaneous and endothermic. This study is expected to help expand the type of supported ionic liquids and their application in the treatment of dyes pollution.

2.7.13 Fungus aspergillus flavus

Aspergillus flavus was employed for biodegradation of BPB by Singh & Singh, [73]. Potato Dextrose Agar medium was used to investigate the biodegradation of dye compounds by fungus. The fungus showed positive results for the degradation/ decolourization for textile dyes. Degradation of dyes was evaluated by the change in the original colour and visual disappearance of colour from the fungus treated Petri plates. Degradation and decolourization of dye were observed by the presence of colour in the fungal mycelium. The addition of BPB in the culture medium adversely affected the growth of *Aspergillus flavus* when compared to their respective controls.

2.7.14 Silica-based aerogels

The silica-based aerogels and xerogels studied by Durães et al. [77] exhibit mesoporous structures with high surface area and tailored levels of hydrophobicity/hydrophilicity. The xerogel with intermediate wetting behaviour shows good removal efficiency and pseudo-second-order adsorption kinetics. Hydrophobic interactions characterized the adsorption process while the monolayer formation was the rate-limiting step. Aerogels were used as adsorbents for several phenolic compounds. The hydrophobic adsorbents show higher performances for the adsorbate with higher partition coefficient octanol/water, with favourable isotherms. Hydrophobic interactions play an important role in the adsorption process.

2.7.15 Activated biosorbent phragmites Karka

Parhi et al. [81] investigated the removal of BCG dye from aqueous solution using activated biosorbent Phragmites karka. The BCG adsorption efficiency was increased from 16.05 to 84.2% with an increase in acidity of the solution and maximized at *p*H 5 of solution. A maximum loading capacity of 392.3 mg/g was obtained at ambient condition. Kinetics study showed that BCG adsorption well fit the pseudo-second-order model than the pseudo-first-order kinetic model. The positive value of, ΔH^o 2.49 kJ/ mole obtained by thermodynamic study reveals the endothermic nature of adsorption and ΔS^o 24.87 $J.K^{-1}mol^{-1}$ showed the increase in degrees of freedom of BCG during adsorption. Equilibrium data showed the best fit with Freundlich isotherm and revealed that the adsorption is chemisorption.

2.7.16 *Ziziphus nummularia*

Ziziphus nummularia was used to remove BCG by Shokrollahi et al. [82]. *Ziziphus nummularia* is a plant commonly found in agricultural fields, readily available and inexpensive adsorbent. Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm models were used to interpret the adsorption isothermal data. The adsorption process is dependent on pH and temperature and follows a pseudo-second-order kinetics model. The values of ΔH, ΔS, and ΔG showed that the adsorbent employed has considerable potential as an adsorbent for the removal of dyes.

2.7.17 Chitosan poly (methacrylate) composites

Chitosan poly (methacrylate) composites were prepared and applied for adsorption of BCG from aqueous solutions by Liu et al. [83]. The adsorption isotherm was well described by the Freundlich model, and the maximum adsorption capacity was 39.84μg mg^{-1} by shaking for 40 min at pH 2.0. BCG adsorption kinetics followed a pseudo-second-order kinetic model, indicating that adsorption was the rate-limiting step. The negative values of Gibbs free energy change showed that adsorption was a spontaneous process. The positive values of entropy and enthalpy change indicated that the adsorption of BCG was endothermic. The value of the adsorption percentage was greater than 97% after three times of recycling test and this confirmed that Chitosan poly composites have a great capability for the adsorption of BCG in solutions.

2.7.18 *Bryophyllum pinnatum Kurz* stem powder

Adsorption of Methylene Blue, BCG and Methyl Red were performed in batches on *Bryophyllum pinnatum Kurz* stem powder (BPP) and Activated Carbon *Bryophyllum pinnatum* (ACBP) by Kindala et al. [84]. Adsorption capacities of the two adsorbents were compared to that of commercial activated carbon (CAC) and were evaluated as a function of pH and the dose of the adsorbent. Freundlich and Langmuir isotherms models were used to test the equilibrium data which were best represented with maximum monolayer adsorptions capacities of 255.754 (pH 11.15), 253.807 (pH 3.35) and 195.313 mg.g^{-1} (pH 3.25) for MB, MR and BCG respectively on ACBP. On CAC their capacities were respectively 176.367 (pH 11.15), 342.466 (pH 3.35) and 108.342 mg.g^{-1} (pH 3.25) for MB, MR and BCG. On BPP the adsorption capacities were respectively 61.013 (pH 11.15), 165.289 (pH 3.35) and 51.733 mg.g^{-1} (pH 3.25) for MB, MR and BG. The results show that ACBP has an excellent adsorption capacity compared with the values of BPP and CAC. The results obtained with Langmuir and Freundlich isotherm models provided the best correlation constant. The adsorption kinetics was found to follow a pseudo-second-order kinetic model with the correlation coefficient close to unity.

2.7.19 Chitin nanofibers

Chitin nanofibers as a valuable natural material to remove BCG dye was investigated by Rezaei et al. [85]. The results showed that colour adsorption was pH-dependent. The optimum pH value was and the optimum adsorption was 92.75% at the concentration of 0.4 mgL^{-1}. The optimum adsorbent dosage was 1.5 g A contact time of 10 minutes at 25°C was considered as the best for these two parameters, which indicates the short duration of this treatment.

2.7.20 Almond husk

Bhanuprakash & Belagali, [86] investigated the adsorption behaviour of almond husk concerning crystal violet, BCG, Pararosaniline and Victoria blue. The adsorbent used proved to be effective, with total removal of all dyes above 90%. The removal of Bromocresol green was 97.5%, Crystal violet 96.9%, Pararosaniline 95.6% and Victoria blue 95%. Isotherm model of Langmuir, Freundlich and Dubinin-Radushkevich were considered favourable.

2.7.21 Acid treated activated charcoal

Activated charcoal was prepared from pine tree cones and was treated with 5M HNO$_3$ and HCl solutions. The acid-treated charcoals were used for the adsorption of cobalt ions from aqueous solution and then utilized for the decolourization of BCG dye in an aqueous medium by Khan et al. [87]. The adsorption study revealed that acid-treated charcoals adsorbed 9.063 mg/g of cobalt within 2 hrs. The decolourization study was carried out using UV/Vis spectrophotometry and the results revealed that acid-treated charcoals decolourized 16.85% of the dye while Cobalt acid-treated charcoals decolourized about 40.5% of the dye within 12 hrs.

2.7.22 Raw bentonite clay and activated carbon from *Acheilia Nilotica*

Abdulganiyu & Ibrahim, [88] investigated the adsorption of BCP onto raw bentonite clay and activated carbon from *Vachellia nilotica* using batch adsorption process. The pseudo-second-order kinetic exhibits the best fit with a correlated coefficient (R^2) close to 1. Experimental values 7.197 mg/g and 5.169 mg/g for Raw Bentonite Clay and activated carbon from *Vachellia nilotica* are closer to the estimated values 7.246 mg/g and 5.263 mg/g. The negative values of change in Gibbs free energy indicated a spontaneous process. Positive values of enthalpy confirm the endothermic character of the adsorption process. Lower ΔH values of 11.01 and 11.98kJ/mol for adsorption of dye onto raw bentonite clay and activated carbon respectively, suggests that the adsorption is physical in nature. New bentonite carbon composite was prepared and characterized by Shalabi et al. [89]. The adsorbent dose was 20 gL^{-1}. The equilibrium between the adsorbate and adsorbent was practically achieved in 90 minutes at pH 1.0. Adsorption kinetics followed a pseudo-second-order rate expression and equilibrium adsorption data of BTB dye on bentonite carbon composite was best represented by the Langmuir isotherm.

Table 3. Maximum adsorption capacities of agricultural, industrial solid and nanoparticle-loaded based activated carbons for Bromocresol green (BCG)

S/N	Adsorption	Adsorption capacity, q_{max} (mg/g)	Isotherm study	Kinetic study	Thermodynamic study	pH	Initial dye Conc. (mg/l)	Equilibrium time (min)	Dosage of Adsorbent (g/L)	References
1	Ziziphus nummularia	6.25	Freundlich	PSO	endothermic	2.0	50	8	0.4	[82]
2	Bryophyllum pinnatum Kurz stem powder	51.7330	Langmuir and Freundlich	PSO		3.25				[84]
3	Extractive Spectrophotometric Determination					4.0		5.0		[90]
4	Almond husk	97.50%	Langmuir			7.0		300	1.0	[86]
5	Activated Biosorbent Phragmites Karka	392.30	Freundlich	PSO	endothermic	0.5	50	300	1.0	[81]
6	Chitosan Poly (methacrylate) Composites	39.84	Freundlich	PSO	endothermic	2.0		40	0.1	[83]
7	Activated carbon	0.0209	Langmuir			5.5		30	0.1	[91]
8	Chitin Nanofibers	18.02				6.0	0.4	10	1.5	[85]
9	Acid-treated activated charcoal	9.063					400	120	0.030	[87]
10	Modified Agricultural Waste	0.0439	Langmuir	PSO	exothermic	2.5	50	60	2.5	[82]

Key: PFO- Pseudo first order and
PSO- Pseudo second order

Table 4. Maximum adsorption capacities of agricultural, industrial solid and nanoparticle-loaded based activated carbons for Bromocresol purple (BCP)

S/N	Adsorption	Adsorption capacity, q_{max} (mg/g)	Isotherm study	Kinetic study	Thermodynamic study	pH	Initial dye Conc. (mg/l)	Equilibrium time (min)	Dosage of Adsorbent (g/L)	References
1	Silver Nano Particle							40		[92]
2	Bentonite Carbon Composite Material	0.0708	Langmuir	PSO	exothermic	2.0	20	60	30	[93]
3	Photolysis, Acetone/UV and H_2O_2/UV			PFO						[94]
4	Several Photochemical Processes					3.0	25	120		[95]
5	Raw Bentonite Clay and Activated Carbon	7.246	Langmuir	PSO	endothermic	3.0	20	45	2.5	[88]

Key: PFO- Pseudo First Order
PSO- Pseudo Second Order

Table 5. Maximum adsorption capacities of agricultural and industrial solid for Bromothymol Blue (BTB)

S/N	Adsorption	Adsorption capacity, q_{max} (mg/g)	Isotherm study	Kinetic study	Thermodynamic study	pH	Initial dye Conc. (mg/l)	Equilibrium time (min)	Dosage of Adsorbent (g/L)	References
1	Mild Steel in Acidic Medium	-3.58	Langmuir		exothermic			7 days		[74]
2	Soil Borne Fungi					7.0	0.05%	8 days		[96]
3	Sawdust Treated by Polyaniline	52.699	Freundlich	PSO	endothermic	3.0	100	4		[97]
4	Bentonite Carbon Composite		Langmuir	PSO	exothermic	1.0	10	90	20	[89]
5	Anodic oxidation			PFO		3.0		60		[98]
6	Raw Maize Cob	0.546	Temkin	PSO	exothermic		100	110	1.5	[31]
7	Modified Cellulose Fibres	38	Freundlich	PSO	exothermic	4.0		120	0.1	[99]
8	Latvian Sphagnum Peat Moss	13.947	Langmuir	PSO	exothermic	7.5	150	120	0.5	[100]

Key: PFO- Pseudo first order and PSO- Pseudo second order

2.7.23 Bentonite carbon composite material

El-Dars et al. [93] investigated the adsorption of Bromocresol purple, and methylene blue dyes onto bentonite carbon composite. The results show that the optimum conditions for removal of BCP, and MB dyes were 30 and 40 g/L respectively. It was further shown that the equilibrium between the adsorbate and the adsorbent was practically achieved in 60 min for both BCP and MB dyes. The results verified that adsorption kinetics followed a pseudo-second-order. Experimental data were best fitted in Langmuir isotherm.

2.7.24 Photochemical processes

Photochemical processes have been widely used in water decontamination process coupled or not with Ultraviolet light. In an extensive investigation, Bousnoubra et al. [95] studied the ability of some photochemical processes in the absence of light (Fenton) and in its presence (photo-Fenton) to remove BCP from aqueous solution. The results showed that the optimal value of pH was 3.0. The most favourable ratio of H_2O_2 to iron was 10:1 for the oxidation state of iron II. Photo - Fenton process at 254 nm is more efficient than that used at 365 nm and Fenton. The efficiency of the processes studied decreases in the following order: Photo-Fenton 254 nm>Fenton>photolysis 254 nm. In general, photo-Fenton appeared suitable for the degradation of the dye since they reinforce the production of radicals OH. These investigations showed that these processes might be used for the treatment of wastewater in industrial scale.

2.7.25 Photolysis, acetone / UV and H_2O_2/UV

Djebbar et al. [94] tested some photochemical processes to decolourize two dyes, taken in mono and binary systems in an aqueous homogeneous medium. Both substrates were treated separately by direct UV photolysis at 254 nm. The experimental results indicated that the methyl green decolourization rate was 66% for a reaction time of 30 minutes. BCP process was 25% for the same reaction time. Total decolourization was obtained for BCP and MG when both substrates were treated by either acetone/UV or by H_2O_2/UV. Meanwhile, the treatment of the mixture became rather complicated compared to the separated dyes. Decolourization process decreased as the concentration of the solution became high. Under these conditions, the solution was not permeable

to UV radiations. Thus, among these processes, acetone/UV was the best system in comparison to the direct UV photolysis and H_2O_2/UV. Additionally, the decolourization process due to direct UV photolysis, Acetone/UV, and H_2O_2/UV was correctly described by pseudo-zero-order and by pseudo-first-order models for each dye taken separately. In the mixture, the latter model remained almost unchanged.

2.7.26 Silver nanoparticle, ferrous sulfate and hydrogen peroxide

Photo-degradation technique offers good potential to remove the colour from wastewater. These methods were employed for the removal of Carminic acid and BCP by Sawsan, [92]. Comparison between the removal of dyes by hydrogen peroxide, ferrous sulphate and silver nanoparticle was studied in sunlight effect. The results showed that decolourization of investigated mordant dyes was feasible to be decolourized by Fe^{+2} process, silver nanoparticles and H_2O_2. Decolourization efficiency of the investigated dyes by Fe^{+2} was better than that of the adsorption process. The techniques were very useful and cost-effective for better removal of dyes.

2.7.27 Sawdust treated by polyaniline

Sawdust and sawdust/polyaniline composite have been tested for the removal of BTB dye from aqueous solutions using batch adsorption technique by Taghried & Abeer, [97]. The adsorption capacity of BTB dye on natural and modified sawdust was analyzed at a pH of 3–4, the contact time of 4min, the temperature of 30°C and initial concentration of 100 mg/L. The results revealed that sawdust coated polyaniline adsorbent has high efficiency to remove BTB dye from the aqueous solution. The percentage removal was 99% as compared with sawdust-coated polyaniline. The adsorption process was spontaneous, endothermic and increased randomness. Freundlich isotherm fit much better than the Langmuir isotherm and obeyed the pseudo-second-order model.

2.7.28 Latvian sphagnum peat moss

The removal of BTB from aqueous solution using *Latvian sphagnum* peat moss was investigated by Said Hassan et al. [100]. *Lativian sphagnum* peat moss is a hydrophilic and biodegradable natural adsorbent. The adsorption equilibrium isotherms, thermodynamics, and kinetics were

studied. BTB showed two removal maxima in acidic (pH 2.5) and almost neutral (pH 7.5) media. Percentage removals at this pH were 80.8 and 88.2%, respectively, while the equilibrium contact time was 120 minutes. The Langmuir and Freundlich models were used to interpret the equilibrium isotherms. The adsorption kinetics showed a more preferred correlation to the pseudo-second-order plot.

2.7.29 Modified cellulose fibres

The in-situ pH-sensitive cellulose fibres were prepared by anchoring BTB molecules on a cationic cellulose fibre through adsorption in an extensive study by Wang et al. [99]. The maximum adsorption capacity was 38 mg/g for 1000 mg/L of BTB / NaOH solution and a dosage of 100 mg for 120 minutes. BTB adsorption on the modified cellulose fibres took after pseudo-second-order kinetics and Freundlich isotherms. The in-situ pH-sensitive cellulose fibres showed a different colour for each pH value from 4 to 8. At the same time, the BTB remained during the pH response, which confirmed that the BTB was hooked firmly on the cationic cellulose fibre. Following this study, a new mechanism for designing a pH-sensitive fibre which may be used in evaluating the freshness of finished product without being polluted has been outlined.

2.7.30 Anodic oxidation on boron-doped diamond electrode

The Anodic Oxidation of BTB on a Boron Doped Diamond anode was studied by Maamara & Bellakhala, [98]. Optimal conditions were fixed at an applied current density of 60 mA cm^{-2}, pH of 3 and treatment time of 60 minutes. Maximum discolouration yielded 99% and total discolouration was observed after 360 minutes, as well as an abatement of 67% of the COD and 59% of the TOC initial value. When applied to effluent containing BTB dye, the colour intensity decreased the COD and the TOC removal reached 94%, 59%, and 52% respectively after 360 minutes. 0.7kWh (g COD)$^{-1}$ and 0.91kWh (g COD)$^{-1}$ were respectively found after 360. The results ensure the effectiveness of the AO treatment using BDD anode, considering it as a promising environmentally friendly technology for the remediation of wastewaters containing BTB dye.

2.7.31 Soil-borne fungi

Jeniffer & Kavitha, [96] analyzed four different soil samples containing leaf litter for potential microbes for the decolourization of dyes. Decolourization of dyes was investigated in the Potato Dextrose Agar medium, with a fixed amount of dye solution (0.5%) in each case being used in the culture medium. Decolourization of dyes was seen and evaluated by the change in the original colour and visual disappearance of colour from the conditioned Petri plates. Optimisation of the physicochemical parameters like carbon source, temperature, and pH was undertaken for the decolourization process by replacing one parameter at a time. Four isolates showed dye decolourization and one isolate was found to be laccase producing organism. The study confirmed the potential of the above isolates in the decolourization of dyes such as MB and BTB and opened scope for future analysis of their performance in the treatment of textile effluent.

2.8 A Critical Assessment of Biosorption Research

Many studies on biosorption had been undertaken, however, emerging challenges in the field have continued to subject researchers to renewed efforts aimed at finding more efficient biosorbents with less cost of production. Biosorption has been identified as a better option in removing dyes from industrial effluents. However, it also has disadvantages such as early saturation of biomass, little biological control over the characteristics of the biosorbents. Further investigation with the aid of modern scientific mechanisms such as process control and modelling will ultimately assist in improving on the present scale of operation for an enhanced process. Most of the existing biosorption studies are targeted at single dye uptake systems while multi dyes sorption systems appear rarely. This may be further investigated. Improvement of immobilization of biomaterials as well as standardizing the parameters involved in the biosorption process and physicochemical conditions including reuse and recycling remain some of the way forward in this instance. The interaction between adsorbate and the adsorbent should be studied to establish the relationships and roles of functional groups in the dye adsorption process.

3. CONCLUSION

Increased production and use of dyes especially in the textile industry has largely contributed to increased environmental pollution. This review

evaluates different agricultural wastes (biosorbents), activated carbon, non-conventional low-cost materials, nanomaterial, composites and Nanocomposites as low-cost adsorbents for removal of BPB, BCG, BCP and BTB from wastewater. These biosorbents have shown considerable adsorption capacity, viable and effective for the removal of BPB, BCG, BCP and BTB from wastewater, hence, biosorption has been established as an effective, cheap, simple and readily available method of removing pollutants especially dyes. However, the majority of the examined works focused on single dye biosorption systems. However, most of the industrial effluents contain more than a single dye thus, it is essential to evaluate the performance of biosorbents in multi dyes solutions. Very little information is available on multi dyes biosorption in binary, ternary, and quaternary systems.

This development, therefore, calls for an approach that will involve the biosorption process using binary, ternary and quaternary based mechanisms. The future development of biosorption requires thorough scientific research and investigation in modelling, regeneration and immobilization of biosorbents and treatment of industrial effluents in order to meet the provision envisaged. It is thus recommended that pilot-scale laboratory experiments of such process be designed and carried out and then up-scaled for industrial application. Besides, in as much as there is more than one class of pollutant in wastewater, effort must be made to modify the biosorbents to be able to remove more than one particular class of pollutants (besides dyes) from wastewater.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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