



Adsorption Materials for the Efficient Removal of Methylene Blue from Wastewater: A Review

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Abstract:

A significant environmental issue has arisen as a result of some enterprises' recent releases of wastewater into the environment that contains high quantities of dyes (i.e. contamination of soil, groundwater, and surface water etc.). The sudden development of the textile industry has led to a concerning scenario where chemicals, such as dyes, are left in treated wastewater, further damaging the environment. Recent research has shown that the use of activated carbon is a very effective technique for eliminating methylene blue (MB) from wastewater. A beneficial source of bio-waste for MB sweeping includes wood scraps, animal-based food waste, and crop residue, as they are extremely effective, reusable, and have solid adsorption capacities. This review paper examines the properties of biowaste-based adsorbents for dye removal, focusing on their efficiency and processing techniques. It also discusses regeneration procedures, financial difficulties, and post-sorption material valuation. The high cost of commercially available activated carbon restricts its supply; hence, researchers are searching for affordable and unexpected sources for adsorbents. This overview provides a comprehensive understanding of recent developments in biowaste-derived adsorbents, emphasizing the need for inexpensive adsorbents for large-scale system optimization.

Keywords: Adsorption, Methylene Blue, Wastewater treatment, Adsorbents, Removal efficiency. Activated Carbon, Dyes, Environment.

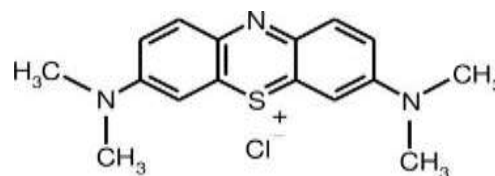
Introduction

ecosystems' ability to support life as a result of decreased sunlight penetration and Current data indicates that over 100,000 dye decreased oxygen levels in the water. The products used for commercial purposes have health risks associated with dye pollution in leaked into the water. The paint, paper, water include the development of skin leather, and printing industries were the next conditions upon coming into contact with the biggest sources of water pollution, after the contaminated water and digestive issues from textile industry. The marine habitat suffers drinking the water, which may increase the when dye is disposed of into the atmosphere, risk of cancer [1]. Human activities and and human wellness is also negatively increasing populations are frequently impacted. The effects may include aesthetic associated with the ecosystem's ubiquity of



problems like discoloration and bad odors in contaminants. Natural resource poisoning is the water, as well as a disturbance of aquatic a sensitive issue globally because of its potential fatal or long-lasting impacts on living organisms. Because they damage a variety of living forms, dyes in wastewater are a serious problem. Concerns about coloring dye contamination are related to both pharmacological and aesthetic issues. Around 100,000 substantially dyed items, or around 10% of the dyes used in industrial applications, amount to 7×10^5 tons of dyes produced each year. That's been discharged into the waters around us, based on recent statistics [2]. Living species on Earth depend heavily on water to survive. The majority of nations, including South Africa, whose surface and subsurface water resources are the primary sources of water, nevertheless struggle with water pollution in spite of the necessity for this resource. Any water that is dangerous for both people and animals to drink can be classified as polluted. The terms "point source" and "non-point source" refer to two different categories of water contaminants: those that originate from moving sources (such as vehicles, buses, and trains) and those that originate from permanent locations (such as mines, factories, power plants, and water treatment stations). When it comes to point sources, water pollutants can be categorized as organic (dyes) or microbiological (viruses and bacteria), or as inorganic (fertilizers and hazardous metals) [3]. Because of its efficiency and large ability to adsorb, activated carbon is a popular adsorbent for color removal from textiles. However, the high running costs, regeneration requirements, and challenges with wastewater separation limit its use. In an effort to reduce the cost of treating

wastewater, researchers are looking at nonconventional alternative adsorbents, such as biosorbents and non-hazardous waste from agricultural and industries [4]. The fabric industry utilizes cationic pigments like methylene blue (MB) to create dye textiles made from silk, wool, and polyester. It is a cyclical aromatic molecule with the molecular formula $C_{16}H_{18}N_3SCl$. A number of harmful side effects, including vomiting, diarrhea, nausea, and burning in the eyes, can be brought on by MB dye emissions. Poisoning can also occur by inhaling the dye or coming into contact with it on the skin[5].



A cationic MB dye's molecular composition:

Methylene blue (MB) is a widely used cationic dye in several sectors, such as textiles, medications, rubber, dyes, and pesticides. Industries that use Congo Red (CR), an anionic azo dye, include textile, printing, dyeing, and polymers. The complicated aromatic structure of MB and CR prevents them from degrading chemically, photochemically, or via biodegradation. Furthermore, wastewater containing dyes is poisonous and may adversely affect humans as well as aquatic creatures and plants, increasing the risk of mutability and carcinogenicity. As a result,



treating the dye-contaminated effluents before disposal is crucial. Consequently, before being released, the dye-contaminated effluents must be treated. There are several techniques for getting rid of dyes, including separate membranes, chemical treatment, sunlight, microbiological treatment, mineralization, and nanofiltration.

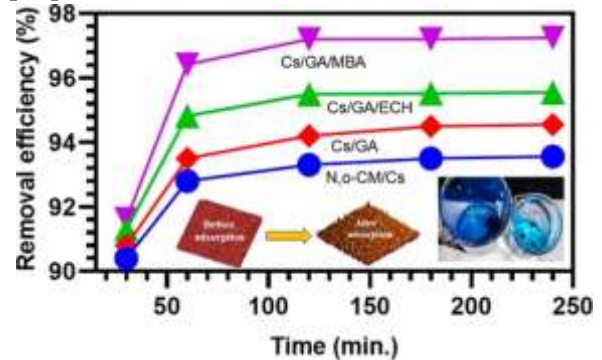
Adsorption has received attention as a viable technique to dispose of waste water containing colors because of its high effectiveness and simplicity of usage. A combination of unfavorable and positive impacts on the adsorption process might result from the simultaneous presence of two or more contaminants in the wastewater. This mostly has to do with the kind of mixture of pollutants there is, how contaminated the area is, and how long the pollutants stay there. Therefore, in order to treat water, one must comprehend the simultaneous binary adsorption process [6]. Methylene blue (MB) is a chemical illustration of a mesoporous adsorbent that acts as an experimental dye for evaluating the elimination capacities of various materials. To recover the dye from wastewater, a number of experiments have been conducted in an effort to develop an effective green dye removal technique. Adsorption is one of the most promising degrading processes since it produces no hazardous byproducts, yields superior results, can be used with a variety of dyes, and doesn't require extremely complex equipment. It is also immune to harmful copollutants found in wastewater. The most often utilized organic adsorbent, activated carbon (AC), has been the focal point of several studies and has strong adsorption efficiency for removing MB. Nevertheless, because of its expensive cost and challenging regeneration process, researchers have been looking for more

affordable and highly efficient adsorbents [7]. Severe ecological issues have been brought on by the world's recent industrial expansion. Additionally, as a result of the growing population and the scarcity of clean water, experts are now looking for other ways to reduce the shortage of clean water. The reduction of polluting components and wastewater cleanup might be the two approaches used to accomplish this. Because of their association with industry, drinking water may include two primary categories of chemical contaminants. This includes heavy metal components such as (Cd (II), Cu (II), Fe (II), Pb (II), Se (IV), Cr (VI), and Co (II)), as well as chemical dyes such as amaranth, tartrazine, methylene blue, and methyl orange. It should be noted that these contaminations lead to the development of cancerous tissue as well as other high-risk disorders such as renal function degradation. Many methods, including membrane filtration, ion exchange, electrochemical technology, adsorption, and zero-valent metal reduction, have been developed to remove heavy metals and dyes from aqueous solutions. Nevertheless, there are drawbacks to these methods, including the inability to retrieve sorbents after usage and the preference for alternative methods of removing heavy metals. New compositions with features like high reusability and simple recoveries should be created to remove these pollutants from water-based solutions in order to solve these problems [8]. Because of the high levels of amino and hydroxyl functional groups in shellfish, chitosan, a biopolymer, has been extensively employed as a biosorbent for the removal of aquatic contaminants. It has been used for a variety of materials, such as composites, powders, and pellets. However, the low surface area

precipitated in a solution of acid that is soluble in water limits its capacity for adsorption. Combining chitosan with a strong substance to create composite adsorbents will increase its adaptability. Although the neem leaf and crab shell chitosan composites worked better, methylene blue was eliminated by the combination of granular activated carbon and shrimp shell chitosan in 94.81% of instances [9]. One of the hazardous cationic dyes that are discharged into textile effluent and have a negative impact on the atmosphere is melanthionium chloride, sometimes referred to as methylene blue (MB) dye. Determining precisely the way a number of chitosan-treated materials absorb MB dye from fictional fluid is the purpose of the present study. Previous research synthesized, characterized, and implemented the claimed chitosan derivatives to extract lead and copper cations from an aqueous solution. Conversely, chitosan has several disadvantages that limit its use in a tidy form. These drawbacks include its tiny specific surface area, poor mechanical properties, and susceptibility to dissolution in acids. It may be altered by techniques including grafting, cross-linking, adding magnetic species and nanoparticles, chemical procedures, and gamma irradiation before being widely utilized in different wastewater treatment. Numerous products have undergone chitosan treatment to eliminate different types of pollutants from aqueous solutions. The study looked at the potential applications of sodium tripolyphosphate and vanillin-modified chitosan-based magnetic Nano sorbents for the removal of different heavy metal cations

from aqueous solutions. Magnetic β cyclodextrin-chitosan/graphene oxide was used as a sorbent to further illustrate the

removal effectiveness of methylene blue generated magnetic mesoporous silica nanoparticles coated with chitosan. Results from this combination were around 84.3 mg/g [10].



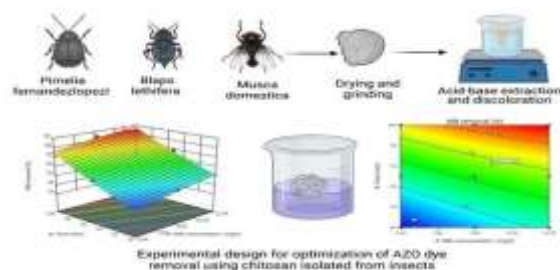
Dyes and waste products from the paper, metal plating, mining, pesticide, and tannery industries, among other sources, are harmful to the environment and human health. For example, huge amounts of trash are produced by mining activities that are loaded with dangerous and toxic metal ions along with certain noble metals, including (Pb, Cd, Cr, Ag, As, Hg, Zn, Cu, Ni, Se, Co, Fe, I, Mn, Mo, and Zn). These metals discharged into the environment and contaminated natural ecosystem. Living things can take up harmful metals since they are soluble in water. Once these hazardous metals enter the food chain, high amounts of them may build up in the human body. As a result, contaminated wastewater containing toxic metal ions needs to be treated before being released into the environment. Methylene blue (MB) is a cationic dye that is used as an indicator, a textile dye, and in other industries. Because of its numerous applications, MB is a common pollutant in the environment and has negative ecotoxicological implications. Toxic metal ions, in contrast to organic contaminants, are known to be carcinogenic and poisonous. The World Health

Organization (WHO) has set water quality guidelines to keep an eye on permissible chemical toxicity levels. Toxic metal ions must be removed from wastewater in order to safeguard the population and surroundings. Although methods such as membrane technology and oxidation have been developed, they are not without constraints, including high maintenance costs and intricate procedures. Due to its low concentration, adsorption of pollutants, ease of use, cleanliness, and convenience, adsorption is a superior solution. Adsorption is a common industrial process used in water purification and happens when a gas, liquid, or solute collects on a solid or liquid surface [11]. The removal of dyes from wastewater can benefit from the use of plant-based adsorbents, such as wheat, rye, rice, peanut husks, maize cobs, Jerusalem artichoke stems, charcoal, and biomass, because they are readily available. These natural polymers work well as adsorbents because of their inherent qualities. They have a large surface area, plenty of functional groups, and electrostatic interactions that allow them to effectively bind and extract color molecules from wastewater. Naturally occurring materials, including crab and lobster shells, shrimp exoskeletons, and insects, are good sources of chitin and chitosan, which have great potential as cheap adsorbents. With their ability to reduce waste and maximize the use of insect carbon dioxide, insects in particular can offer a sustainable supply of chitosan. Magnetically modified nanoparticles containing certain groups make separation with a magnetic field simple. By adjusting their surface characteristics or functional groups, polymeric adsorbents such as resins and gels can be made to better absorb dyes. Different applications and

operating situations might benefit from the distinct characteristics and adsorption processes that each adsorbent provides. Adsorption capacity, cost, availability, and the particular needs of the wastewater treatment process all play a role in choosing the best adsorbent [12].

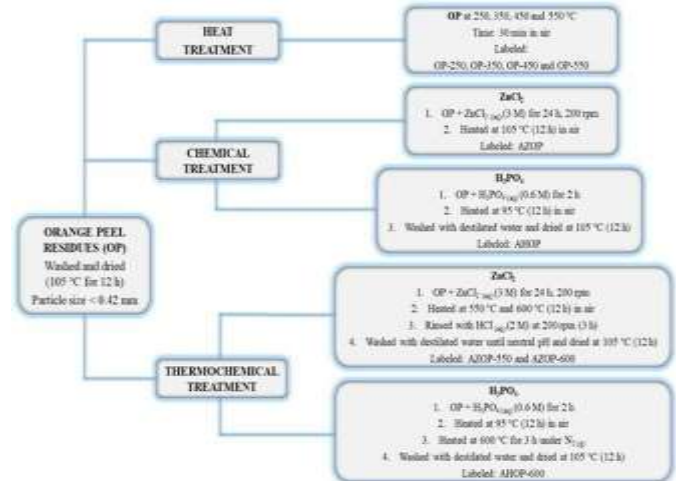
Experiment

We obtained the following materials from Biochemist Chemosphere: sodium hydroxide (NaOH, 97%), hydrochloric acid (HCl, 99%), hydrogen peroxide (H₂O₂, 98%), and methylene blue dye (MB, C₁₆H₁₈ClN₃S, 82%). Chitosan was extracted from insects that served as a variety of local resources and are widely distributed both globally and in Algeria. The insects used in the field study were not protected or threatened species, and they were obtained in a dead and dry condition. No special permission was needed to access the study site. At an initial MB concentration of 12.79 mg/L, the dye removal effectiveness ranged from 35.9% to 88.7% for CS-BL, 18.8% to 47.1% for CSPF, and from 10.3% to 29.0% for CS-MD, according to the experimental work and statistical computation of the CCD. At a reaction time of 120 minutes, the maximum methylene blue dye removal effectiveness for CS-BL was 88.7% [13].



Methodology of absorption process:

Each batch absorption test used each 250-mL Erlenmeyer flask holding 50mL dye solutions and dry biomass. The flasks were shaken at 150 rpm for 180 minutes to ensure equilibrium. The experimental parameters of initial MBD concentrations (5, 10, 15, 20, and 40 mg L⁻¹), contact times (10, 20, 30, 40, 60, 90, 120, and 180 min.), pH values (2, 4, 6, 8, 10, and 12), and temperatures (303, 313, 323, and 333 K) were also conducted to determine the effects of the sorption factors of adsorbent dosage (0.05, 0.1, 0.2, 0.4, and 0.8 g L⁻¹). The adsorption isotherm determines the sorption capacity residual concentration and the adsorbate fixed temperature. An initial MB dye concentration solution containing 5, 10, 20, 30, and 40 mg L⁻¹ was mixed with 0.1 g of adsorbent for three hours at pH 6 in batch sorption studies, which were carried out at 303 K. The mixture was then agitated at a velocity of 160 rpm. Next, we looked for any remaining MBD content in the reaction mixture. Langmuir. An analogous methodology was applied to the kinetic experiments at pH 8. Initially, 50 mL of MBD solution (10 mg L⁻¹ concentrations) and 0.1 g of adsorbent were combined separately. The combination was then produced and heated to 298 K for the necessary intervals of 10, 15, 30, 120, and 180 minutes. It was determined how much MBD was present in the clear solutions [14].



For this investigation, orange peel (OP) was gathered following the consumption of orange juice. The residue was dried in an oven at 105 °C for 12 hours after being repeatedly cleaned with distilled water. After that, the material was pulverized (particle size less than 0.420 mm), chopped into little pieces, and stored. Thermal, chemical, and thermochemical processes were used to alter the biomass of OP. Initially, an oven set to 250, 350, 450, and 550 °C for 30 minutes was used to heat treat the OP biomass in order to convert it. The materials that were produced were given the labels OP-250, OP-350, OP450, and OP-550, in that order. The reaction was carried out with ZnCl₂ and H₃PO₄. Utilizing various analysis methods, the materials' physicochemical characterization was carried out. Proximate analysis and elemental analysis were performed to evaluate OP composition. The active functional groups were investigated by Fourier transformed infrared spectroscopy (FT-IR) in the 4000 to 450 cm⁻¹ range using a Spectrum two-PerkinElmer with UATR, while the surface area was determined using the BET technique (Brunauer, Emmett, and



Teller). While the salt addition technique [31] was used to estimate the pH of zero-point charge (pHPZC), Boehm's approach was used to quantify the materials' acidic and basic surface functional groups [15]. A 100mL volumetric flask was filled with about 0.1 g of methylene blue (C₁₆H₁₈N₃SO₃ · 3H₂O), which was then diluted to the appropriate amount with deionized water. In a 250-mL volumetric flask, 0.5 mL of the stock solution was pipetted out, and the volume was adjusted by adding deionized water. In order to treat a single adsorbent, glass wool was first placed within the column to serve as the adsorbent's support. The water-soaked adsorbent was added to the column, and the water was then let to flow through it. This process allowed colored compounds and dissolved components to be removed from the adsorbent. To fully remove these undesirable materials, a few more milliliters of deionized water were added.

Then this water was emptied. An investigation was conducted on the impact of treatment flow rate on methylene blue removal. The graphic makes it rather evident that as flow rate increases, removal efficiency falls. Slightly more than 98.43% of the methylene blue was eliminated at a flow rate of 1.0 mL/min, whereas 96.61% and 91.86% of the methylene blue were eliminated at 1.4 and 1.8 mL/min, respectively.

Methylene blue in the sample solution may have had more opportunity to come into contact with the adsorbers' active surface when the flow rate was slow, which might account for these observations. However, because it speeds up the elimination process, a flow rate of 1.4 mL/min was used for the subsequent studies [16]. Zeolites are naturally occurring porous aluminosilicates

connected by common oxygen atoms. These aluminosilicates have a range of cavity layouts. The zeolite has several different species [17]. Balazite and clinoptilolite are examples of natural species. Nevertheless, because of its high selectivity for certain contaminants, clinoptilolite, a heulandite mineral, is the material that is studied the most. Due to its unique cage-like structure, zeolite is ideal for eliminating trace contaminants such as heavy metal ions and phenols. Because microbial adsorbents can treat stormwater containing dyes in an ecologically safe manner, they are a viable method of detoxifying wastewater, including nonliving material. Alcohol, aldehydes, ketones, carboxylic, ether, and phenolic chemicals are among the specific surface chemistry of microbes that affect how well colors are removed. Chelation and complexation processes are employed to achieve dye sorption using biosorbents such as chitin, peat, chitosan, yeast, and fungal biomass. Enormous surface area, high adsorption capacity, huge porosity, stability, compatibility, eco-friendliness, ease of regeneration, and excellent selectivity in eliminating various dye types are all desired characteristics of good adsorbents. Biochar's adsorption capacity and hydrophobicity are determined by its pore volume and dye functional groups.

Conclusion:

The most abundant commercial source of carbon synthesis is bio-waste, which is frequently converted into activated carbon. Bio-waste has become a cheap, efficient, and sustainable source of activated carbon for MB removal between 2012 and 2021. The beginning prices, local availability, stability, environmental friendliness, transportation,

applicable treatment methods, recycling, longevity problems, regeneration potential, and pore volume after deactivation are some of the characteristics and definitions of lowcost bio-waste-derived adsorbents. The pH level is the most important factor influencing the adsorption of cationic dyes when it comes to performance criteria; high pH levels are required to obtain maximal dye absorption. The factors that affect the dye-adsorption capacity also include the initial dye concentration, temperature, adsorbent type, dosage, and time of contact. The adsorption investigations utilize a variety of processing techniques, such as chemical, carbon dioxide, and steam activation. While chemical activation yields the largest porosity and surface area, steam activation is the most economical method. There are several desorption techniques for regeneration procedures, such as vacuum, organic solvent, thermal acid and nitric acid, sodium hydroxide, and biological methods. The amount of adsorbent utilized, how easy it is to prepare or process, green chemistry concepts, and the activation process may all be taken into account when designing a costeffective system. In addition, post-adsorption material management appears to benefit from the use of fertilizer, catalysts, and ceramic materials.

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