

A Review on Effects of Operating Parameters in Batch and Column Mode for Adsorption of Methyl Violet Dye

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Abstracts: Direct discharge of industrial effluents without treatment into natural sources poses a significant risk to the environment. Dye compounds are toxic and difficult for nature to process, causing serious physiologic harm to all organisms that come into contact with them. Water quality is directly impacted by the presence of methyl violet (MV) dye pigments as it reduces the photosynthetic activity of the streams, so it is crucial to eliminate it. Adsorption is generally accepted as a reliable method for getting rid of dye in wastewater. In most cases, the adsorption process is aided by the mutually beneficial interactions between the adsorbent, the dye, and the adsorption environment. This review highlights current scenarios of MV removal by various low-cost, eco-friendly adsorbents, and their efficiency. The removal of MV is examined in depth in this review paper, which discusses a variety of batch and column adsorption design experiments. Several parameters influence the adsorption process, which is the foundation of all laboratories looking for the best conditions. The primary goal of this review is to provide current information on the most researched affecting factors for batch and column operating modes. Flow rate, dye concentration, and bed height are all parameters in column adsorption investigations and contact time, pH, temperature, particle size, agitation speed, and adsorbent dose were all compiled for batch adsorption investigations and summarized in this review.

Keywords: Adsorption, Batch Mode, Column Mode, Adsorbent, Agro-Waste, Methyl Violet.

1. INTRODUCTION

The rapid advancement of numerous technical disciplines has led to a surge in environmental disruptions and major pollution challenges, including the contamination of enormous amounts of water [1,2]. Because of the lack of available water sources, water contamination has emerged as one of the world's most pressing environmental problems [3]. The textile sector has undergone a period of transformation in recent years. As a large variety of high-quality dyes and color pigments were available, the textile industry began producing massive amounts of colored effluents [4]. The coloring of finished products in a variety of industries, including textiles, cosmetics, food, paper, rubber, plastics, and pharmaceutical polymers, is frequently accomplished with the assistance of organic dyes [5-7]. When dyes and other chemicals used in the textile industry leak into waterways, it can have devastating effects on aquatic ecosystems [8]. Even after being subjected to basic, secondary, and tertiary treatment, textile industry effluents still include dissolved pollutants and dyes. The removal of harmful dye and pigments from wastewater is made more difficult by the fact that many of the conventional treatments are less successful [9,10]. These colors restrict light penetration, increase toxicity, and cause gene mutation, cancer, dermatitis, and allergies, which harm

aquatic plants' photosynthesis [11,12]. Since the beginning of time, the dye has been put to use in a wide variety of businesses, including those dealing with pulp and paper, textiles and plastics, leather, cosmetics, and food [13-15].

Dye compounds are pigments that bind strongly to one material or another. Fabrics, leather, paper, hair, and other materials can all be colored with a liquid dye solution. The substrate needs to be either completely or partially soluble in the dye solution. Dye classification depends on their chemical composition or method of use [16,17]. When it comes to the process of application, dye molecules are meticulously crafted to ensure they have the necessary characteristics. This allows the dye to be utilized to its full potential [18]. Dye molecules created specifically for use in textiles are designed to build a strong bond with the fiber molecules to which they are applied [19]. Protein fibers are colored using acid, mordant, and vat dyes, while cellulose fibers are colored with direct, reactive, and vat dyes [20]. Color acrylic fibers with dispersion or basic dyes. Most synthetic dyes are organic compounds with a very intricate molecular structure, and they are made to be robust against the effects of common chemicals and organisms. Thus, these colors have excellent stability and durability [21].

Cationic dye methyl violet has many important applications as a pigment, textile dye, and printing ink. Textiles, wood, bamboo, leather, and even straw can be colored with MV [22]. Therefore, it is crucial to use an appropriate treatment strategy to prevent the emergence of MV in the environment. Over the course of several decades, numerous methods have been investigated for removing dyestuffs from wastewater, including chemical oxidation, electrochemical treatment, coagulation, biological degradation, ozonation, nanofiltration, reverse osmosis, advanced oxidation processes, and photocatalytic degradation [23-26]. However, there are still gaps in each technology that prevent it from reaching its full potential in terms of efficiency, harmless processing, and cost management. Adsorption, on the other hand, is an efficient technology for wastewater treatment because of its low cost and ease of usage with respect to a wide variety of pollutants. Adsorption does not degrade the complex organic molecules; hence it does not produce any hazardous byproducts [27].

Economic adsorbents for the removal of various colors from wastewater are receiving a lot of interest at the moment. Toxic colors in water can be removed using a number of different adsorbent materials [28]. Suitable adsorbents are extensively utilized and accessible for the removal of dye contaminants from wastewater. Based on their origin, structural composition, and processing conditions, these materials had unique surface attributes such as pore volume, size, functional groups, surface area, and charge [29,30]. Adsorbent materials made from agricultural wastes have recently found widespread use in the field of dyes removal from wastewater, because to a number of benefits over more conventional materials, including lower costs, greater efficiency, biodegradability, and the use of renewable resources [9,10]. Regardless of where you are on the planet, you'll need to look for an adsorbent material that works well, is cheap, and has great surface qualities. Agricultural byproducts have the greatest potential as a sustainable resource for adsorbents [23,27]. To remedy this, a wide range of effective adsorbents were manufactured from various forms of biomass, agricultural by-products, and agricultural solid wastes. This review article is a summary of the findings of several studies that analyzed the capability of various adsorbents to remove various dyes. The primary purpose of this review is to give the most recent information on the factors that have received the greatest research attention regarding batch and column operating modes.

2. METHYL VIOLET (MV) DYE: CHARACTERISTICS AND EFFECTS ON HUMAN HEALTH AND ENVIRONMENT

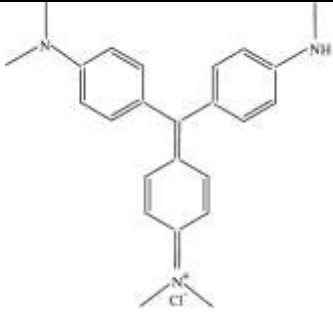
Dyeing is a common practice in many industries, including those dealing with cotton, textiles, plastics, food, automobiles, boats, paint, coatings, and paper [11,24,31]. Dyes are difficult to biodegrade because their chemical compositions and synthetic origins make them very resistant to light and oxidation. Most dyes are extremely dangerous carcinogens that may withstand and even thrive in the conditions of their use, posing a serious threat to human and environmental health [32]. Dyes applied to the surface water reduce the quantity of photosynthetic activity in aqueous media by blocking the sun's rays.

Methyl violets are an important group of chemical compounds employed as colors. The dye's hue can be adjusted by adjusting the quantity of methyl groups connected to it. Its primary function is as a deep purple dye for textiles; however, it is also used to color paintings and inks [32]. The photosynthesis of aquatic plants is inhibited by

the cationic dye MV, which also happens to have an extremely brilliant and intense color. Skin and eye irritation can occur after prolonged exposure to MV. The methyl group count that took the place of the amine hydrogen is what gives MV its color. It has been shown to be harmful to most animals, yet it can be used as a mediocre disinfectant on occasion. While ingestion of MV typically aggravates the gastrointestinal tract, inhalation of MV may aggravate the respiratory system [33].

MV has been identified as a hazardous chemical or material and its usage has been banned in the aquaculture and food industries because of the harm it causes to human health [34]. However, its low cost, ready availability, and efficacy mean that it is still used in some locations. Moreover, the product's inclusion of a cationic dye which is very poisonous to mammalian cells has been linked to significant eye irritation, severe sensitization to light, and irreversible harm to the cornea and conjunctiva [35-36]. However, in severe situations, it might cause respiratory and renal problems. The aesthetic value, gas solubility, and water transparency may all be negatively impacted by the discharge of such a huge quantity of dye with wastewater into aquatic resources. Bioremediation technologies, which are directly tied to the commitment to sustainable development, offer hope in the face of this complicated setting, which presents deep repercussions to ecosystems and to human beings [37]. Table 1, shows the basic characteristics of MV.

Table 1. Characteristics of MV

Appearance	Green to dark-green powder
Chemical structure	
Molecular formula	C ₂₄ H ₂₈ N ₃ Cl
Molar mass	393.96
Melting point (°C)	137
Boiling point (°C)	532.2
Absorbance (nm)	587

3. AGRO-WASTE: POTENTIAL LOW-COST ADSORBENTS

Agro-waste refers to the waste that is typically produced as a by-product of agricultural activities. For example, the peels of fruits and vegetables, the leaves of plants, and the inedible parts of vegetables are all examples of agro-waste that cannot be utilized for anything else or sold because they do not have any monetary value [22,25,38]. Waste from agriculture is a significant disposal challenge for the food industry. Some of the garbage we generate is biodegradable and might be used for composting, but we generate it at such a high rate that it's a hassle to keep up with [39]. Agriculture generates garbage and uses important agricultural soils. These items are agricultural leftovers that are not typically sold on their own. These byproducts may contain compounds of human utility, but the cost to collect, transport, and treat them for human consumption far exceeds their economic value [40]. Due to their negligible or nonexistent commercial value, agricultural waste products are notoriously difficult to dispose of. It is essential that materials used in agricultural production be recycled [41]. Figure 1, represents the classification of low-cost adsorbents.

There are a number of aspects to consider when deciding which precursor to use in the creation of inexpensive adsorbents. The precursor should not only be cheap and safe to use, but also widely available. In addition, the adsorbent moiety's high carbon or oxygen concentration is crucial for effective adsorption. excellent abrasion resistance, excellent heat stability, and small pore sizes all contribute to a large amount of exposed surface area

and a large adsorption capacity [42]. Studies on a variety of agricultural waste items are being conducted to establish the optimal conditions for MV removal from aqueous solutions [43-45]. On the other hand, as a substitute for adsorbents that are more costly, locally produced agricultural waste products that have high pollutant binding capacities have been proposed and researched. Different agricultural waste materials have varying capacities for removing MV, as shown in Table 2. Adsorbents made from raw or processed agro-waste can be used to remove of MV.

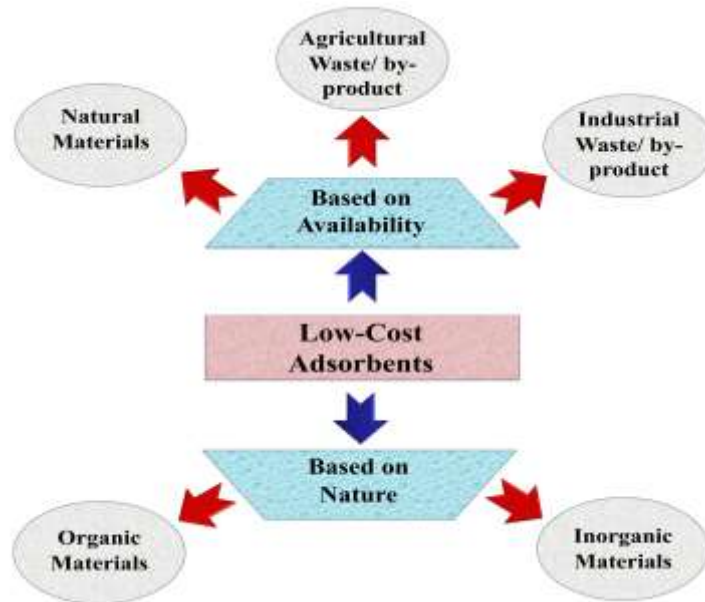


Figure 1. Classification of low-cost adsorbents

Table 2. Different agricultural waste materials adsorption capacities

Adsorbent	Dye	Adsorption Capacity (mg/g)	Reference
Hyacinth	MV	6.67	[46]
Date Seeds	MV	59.50	[47]
Sawdust AC	MV	531.16	[48]
Waste Paper	MV	4.30	[49]
Granulated Mesoporus Carbon	MV	202.80	[50]
Coconut Husk Powder	MV	454.54	[51]
Sugarcane Bagasse	MV	107.50	[52]
Coffee Husks	MV	12.24	[53]
Blue Green Algae	MV	13.41	[54]
Peanut Husk	MV	20.95	[55]
Ceiba Pentandra Sawdust	MV	15.33	[56]
Kaolin	MV	74.03	[57]
Modified Palm Fiber	MV	529.76	[58]
Corn-Cob AC	MV	40.81	[59]
Raw Carobs	MV	9.80	[60]
Modified Carobs	MV	62.50	[60]
Tea Waste NPS	MV	200.00	[61]
Lemon Wood AC	MV	23.60	[62]
Tamarind Seeds AC	MV	18.58	[63]

Morocco	MV	625.00	[64]
Brown Algae	MV	10.02	[65]
Cardboard Waste	MV	78.12	[66]

The treatment of water and wastewater, as well as the management of waste, can benefit from the utilization of agricultural waste as adsorbents. It has been demonstrated that using agricultural waste as adsorbents is beneficial. Large quantities of agricultural waste products are generated, despite the fact that these goods have little value from a monetary standpoint; as a result, they are a burden on the environment [67]. When compared to several other costly adsorbents that are based on different materials, they are considered to be the best option. Figure 2, represents the raw material processing schematic approach.

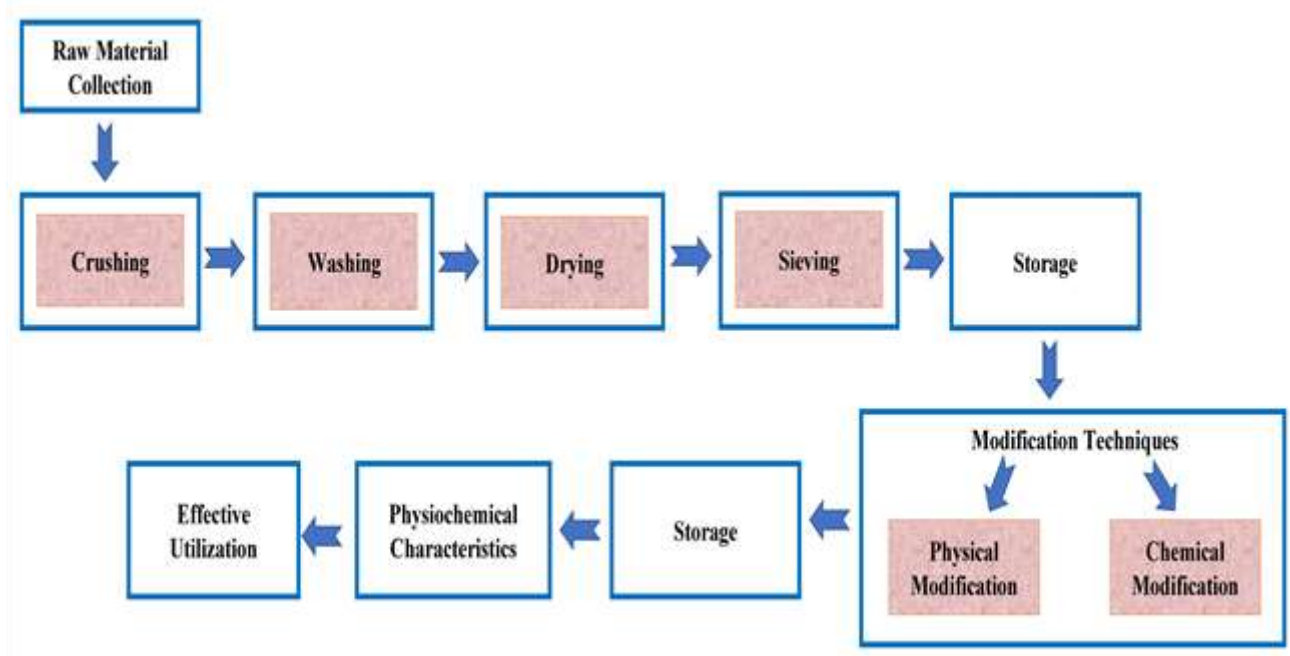


Figure 2. Raw material processing schematic approach

4. ADSORPTION MECHANISM

Adsorption is a surface phenomenon because it increases the concentration of molecules on the surface of a liquid or a solid. The adsorption process requires both the adsorbent and the adsorbate [40]. The adsorbent is the substance on which adsorption takes place, as opposed to the adsorbate, which is the material that is adsorbed on the surface of the adsorbent [41]. Adsorption occurs when forces at the surface of a liquid or solid phase are weak or unequal. Because all molecules are attracted equally from all sides, there is no net force felt by any molecule in the bulk [42, 68]. Molecules at the surface experience an inward force as they are pushed into the bulk by the molecules that surround them [43, 69]. Adsorption is a byproduct that cleans textile effluent of cationic, mordant, and acid dyes. The success of adsorption methods in removing steady-state contaminants has contributed to their rise in popularity. The monetary implications of this strategy are likewise manageable. Adsorption-based decolorization relies on two distinct mechanisms surface adsorption and ion exchange both of which are affected by a wide range of physiochemical factors such as the nature of the dye-sorbent interaction, the sorbent's surface area, particle size, temperature, pH, and the length of time the two systems are in contact. Many different inexpensive adsorbent materials have been studied for their potential to remove color [44-46, 70].

Adsorption with activated carbon is a tried-and-true method for treating wastewater by removing organics and certain inorganics, especially in the case of textile finishing waste. It works wonderfully for getting rid of organic solvents and soluble dyes. This treatment approach is attractive because it permits the reuse of treated wastewater

[46]. The treatment expense is justified by the space savings and elimination of sludge buildup. When activated carbon is used to treat wastewater containing both organic and inorganic components, the weak physical forces known as Vander Wall's forces keep the chemical molecules in place on the carbon's surface [47]. Clean water is produced as it passes through the bed. Adsorption is preferred over competing techniques because of its low cost and high efficiency. The high price and associated challenges of activated carbon have motivated research towards low-cost adsorbents. Dye removal using commercially available adsorbents is common and relatively inexpensive [48]. Furthermore, because the adsorption capacities of the various adsorbents are not especially big, further research is still required to identify new adsorbents that are less expensive, more readily accessible, and highly effective [71]. Figure 3 provides a visual representation of the adsorption mechanism.

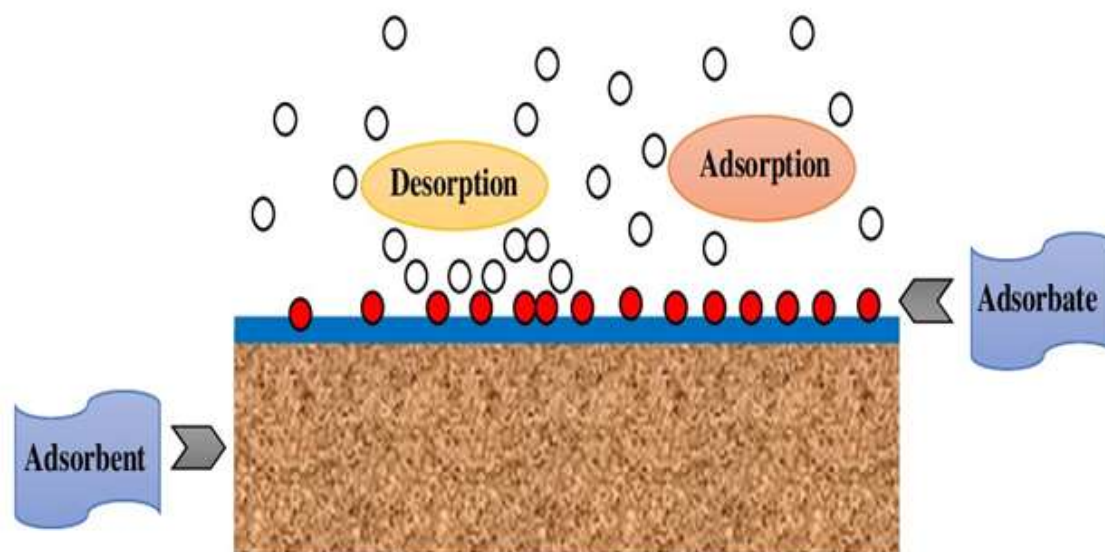


Figure 3. Adsorption mechanism

5. INFLUENCE VARIOUS PROCESS PARAMETERS

The dyes are affected by a number of process parameters, including (but not limited to) the pH of the solution, the concentration of the metal, the rate of agitation, the particle size, the amount of adsorbent, the temperature, and the length of time they are in contact [72]. Adsorption is a highly sensitive method for removing contaminants from the environment, but its efficacy is highly dependent on the initial concentration of the pollutant. Adsorption is greatly influenced by temperature, making it one of the most crucial variables to account for. Adsorption is almost always an exothermic reaction, hence an increase in system temperature results in more adsorption and a higher adsorption rate [73]. However, despite the rising temperature, staff members have noticed an increase in consumption. The amount of substance that can be adsorbed from a solution is strongly influenced by the solution's pH. The adsorption of cations is enhanced and the adsorption of anions is suppressed as the pH of a solution rises [74]. For example, the adsorption capacity of an adsorbent may be significantly affected by its physicochemical parameters, such as its surface area, particle size, and pore volume [75].

The adsorbent concentration determines the surface's binding sites. The percentage of adsorbate eliminated increases with adsorbent dosage. No further adsorbate can be removed after equilibrium [76]. When the optimal solid/liquid ratio is used, the amount of adsorbent used to extract adsorbate ions from the solution is maximized. Adsorption efficiency doesn't change with adsorbent dosage. A system needs "contact time" to reach equilibrium. In this heterogeneous system of solids and liquids, mass transfer occurs in many phases, some of which may be slow [77,78]. Reaching equilibrium requires determining contact time. The main factor in adsorption is pH. The adsorbate content, solution chemistry, and functional group activity on the adsorbent surface alter. As pH increases, metal

adsorption improves. A high initial adsorbate concentration is needed to overcome the bulk phase mass transfer barrier. Loading capacity usually rises with initial concentration [79]. Due to adsorbate ion mobility and solution viscosity, adsorption rates increase with temperature. Thermodynamic factors including enthalpy, entropy, and free energy can be understood by adsorption process temperature research. Size increases particle surface area. More binding sites on larger surfaces. Adsorbent uptake/saturation per unit mass is higher for smaller particles due to lower mass transfer driving power per unit area. To overcome the boundary layer's mass transfer barrier, an adsorbate needs speed. Adsorption increases with agitation speed [80]. Various parameters affect dye removal, as shown in Figure 4.

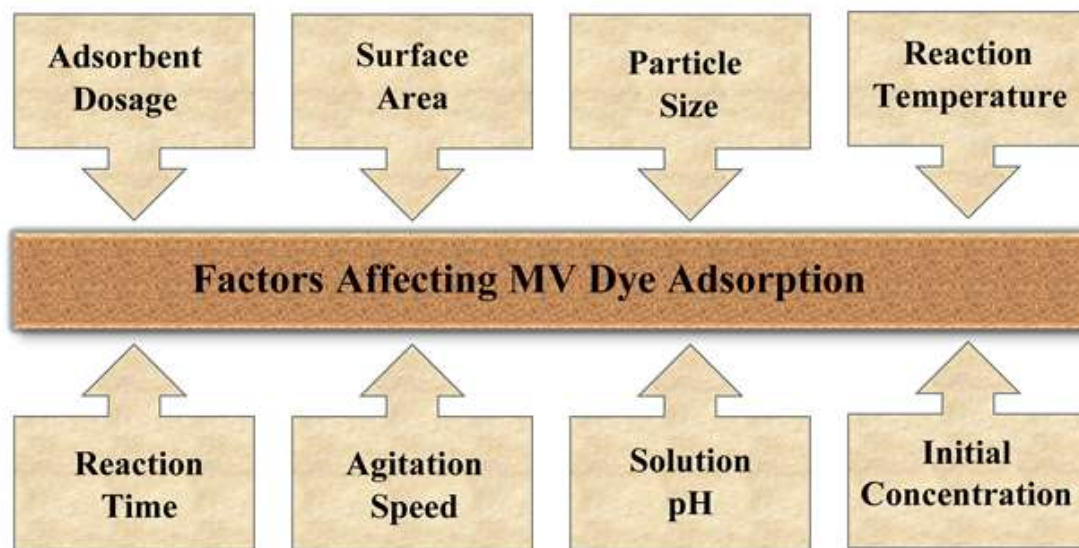


Figure 4. Various factors affecting the dye removal

6. BATCH MODE: ADSORPTION

High-quality adsorption removes dissolved organic contaminants like colours from industrial waste water. Adsorption is material concentration on solid things. Adsorption uses surface forces [34]. When a solution with an absorbable solute, called an adsorbate, contacts a solid with a highly porous surface, liquid-solid intermolecular forces of attraction concentrate the solute at the solid surface. Industrial wastewater pollutant separation chemical engineering procedures include adsorption. Adsorption experiments using different adsorbents are described in depth in column/continuous adsorption studies, whereas batch adsorption studies give crucial information and parameters for removing dyes [63,75]. The parameters that will be adapted for use on an industrial scale employing fixed bed columns can be learned through experiments conducted on a smaller scale as part of the batch research [33,56]. In comparison to batch adsorption, continuous column adsorption is easier to run, the adsorption process is completed more rapidly, and scaling up is less challenging [11,22,50] However, batch adsorption is the preferred method for laboratory-scale investigations since it requires less material and less time in total [57,58]. While batch adsorption is useful for small-scale research, it is not a good fit for large-scale applications. Adsorption can be predicted for performance before it is employed on a larger scale by studying it in batch mode [22,38,49]. The removal efficiency and adsorption capacity of different process parameters are shown in Table 3. Furthermore, the equilibrium investigation provides crucial information on the efficacy of a certain adsorbate-adsorbent system [8,59,71].

In some adsorption processes, equilibrium is not reached because column adsorption times are shorter than batch adsorption times [19,33,70]. Even if it's probable that column adsorption's reduced contact time may render the results of batch experiments inaccurate, they can still be used to predict performance [60]. Because of this, it is of the utmost importance to determine whether or not the adsorbent can be used in a continuous mode of operation.

The batch tank mixes adsorbent with wastewater for a set period and pH, then measures the final concentration. After batch processing, centrifugation, sedimentation, or filtration separate the solution. Industrial batches or crossflow systems require enormous amounts of adsorbent [12,23]. Industry can scale up or down the batch process. After desorption, the adsorbent can be reused for another batch process sequence. Adsorbent absorbs contaminants in the batch tank. Physical and chemisorption can occur. Physical adsorption is reversible because Van der Waals forces attract. Strong chemical connection attracts irreversible chemisorption. Figure 5 depicts the batch mode single-stage adsorption experiment setup/approach for the removal of dyes.

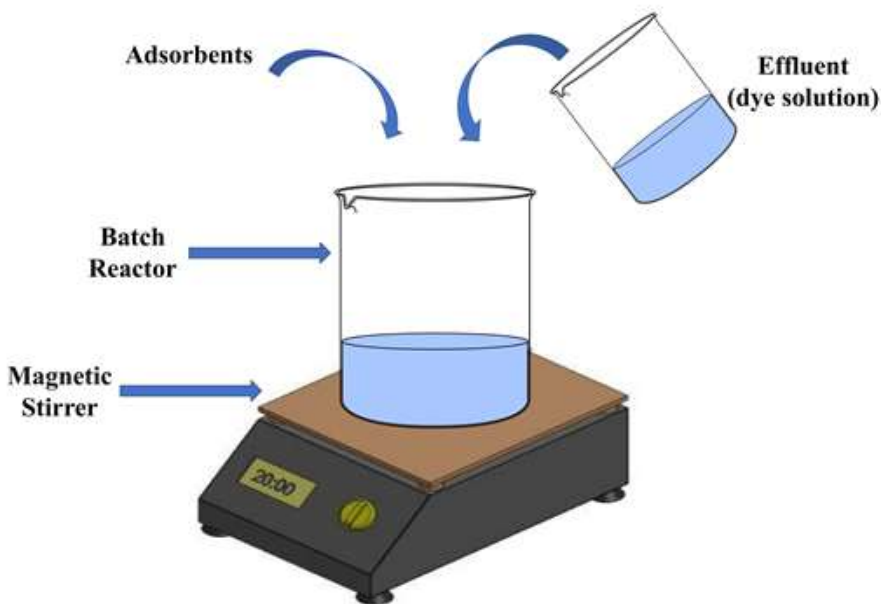


Figure 5. Batch mode single stage adsorption experiment setup/approach

Table 3. Batch mode adsorption of various process factors and removal efficiency

Dye	Adsorbents	pH	Dosage (g/l)	Temp. (°C)	Conc. (ppm)	R.P. M	Time (min.)	Removal Efficiency (%)	Reference
MV	Canola Straw Char	8	0.200	25	10	990	120	95	[81]
MV	Peanut Straw Char	8.9	0.200	25	10	990	120	92	[81]
MV	Soybean Straw Char	9.0	0.200	25	10	990	120	90	[81]
MV	Rice Hull Char	6.4	0.200	25	10	990	120	89	[81]
MV	Almond Shell	6	5	25	20	-	90	84	[82]
MV	Rice Bran Waste	7	2	25	100	150	42.75	97.4	[83]
MV	Banana Stem Biochar	3	0.25	25	60	200	60	95.71	[84]
MV	Cocoa (Theobroma	8	0.1	35	20	125	120	93	[85]

	Cacao) Shell								
MV	Groundnut Shell	6	1	28	50	200	120	85	[86]
MV	Bean Pod	5	1	28	50	200	120	83	[86]

7. COLUMN MODE: ADSORPTION

Information regarding the sorbate-sorbent system's efficacy can be gleaned from the sorbent's sorption capacity, which can be measured in a batch equilibrium experiment [7,11]. However, most treatment systems (such column operations) cannot make use of data collected under batch conditions since contact time is not long enough to achieve equilibrium. Therefore, it is important to evaluate the sorbent's continuous mode applicability [44]. A continuous flow system is an efficient procedure for large-scale wastewater volumes and cyclic sorption/desorption: a fixed-bed reactor is a straightforward approach for calculating bed operating life span and regeneration time in order to get fundamental engineering data. In order to find the experimental breakthrough curve, we employ fixed-bed sorption [4,8,26]. Due to their versatility, low reagent handling, and consequently low operational cost, column systems are widely considered to be an excellent choice for the industrial removal of dyes and/or colored compounds using adsorption techniques performed in column systems [17,77]. There is a lack of literature on the topic of continuous mode fixed-bed column pollutant removal.

Processes that include chemicals and the environment frequently make use of fixed-bed operations. There are many different kinds of reactors that can be used to remove MV from wastewater, such as batch reactors, fluidized bed columns, and continuously stirred tank reactors (CSTRs). However, fixed-bed columns are frequently preferred in adsorption processes [22,35] due to their straightforward design, ease of operation, low cost of fabrication, minimal attrition of adsorbent, high efficiency, and the fact that they can be easily scaled up from a laboratory scale. Adsorption capacity and process variables for column mode adsorption are listed in Table 4. For basic engineering data, continuous flow mode is essential [13,28]. The continuous flow process is adaptable and low-cost. Continuous flow is needed in enormous effluent systems with cyclic adsorption/desorption [50]. Mathematical breakthrough curves predicted column bed lifespan and regeneration. Few papers describe continual metal removal. The breakdown curve can estimate a fixed-bed model's kinetic, according to kinetic models. Industrial effluent contains colors that harm the environment; hence companies use fixed-bed columns for adsorption [67]. Wastewater treatment plants prefer column adsorption as an industry-scale method due to its simplicity and reliability. Adsorption is cheaper, simpler, and easier to design than other water treatment processes [74,86]. Figure 6 depicts the experimental setup of continuous/column adsorption studies performed to remove dyes.

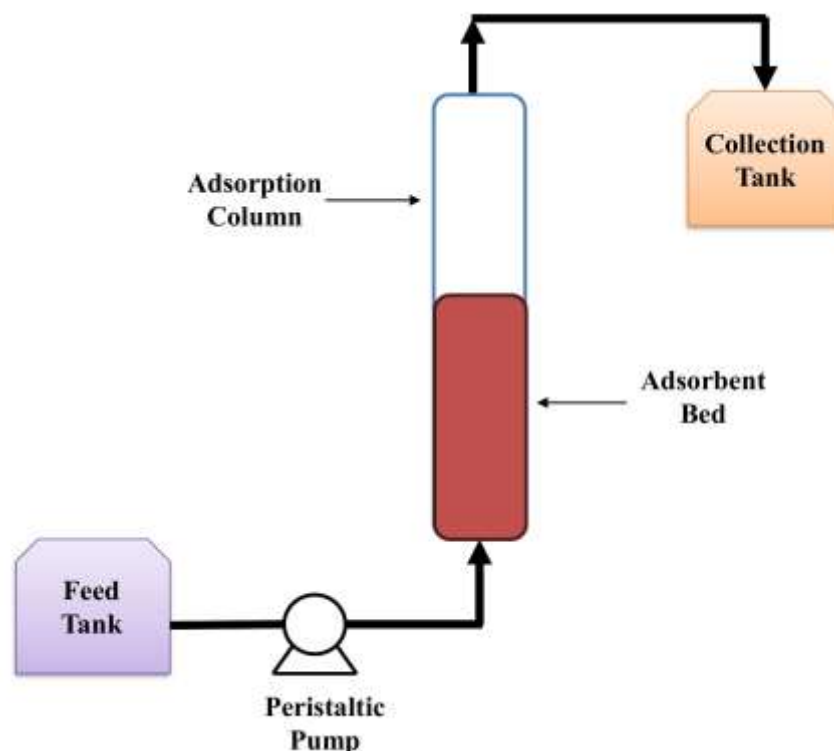


Figure 6. Continuous mode adsorption experiment setup/approach

Table 4. Column mode adsorption various process factors and adsorption capacity

Dye	Adsorbents	Conc. (ppm)	Bed Height (cm)	Flow Rate (ml/min.)	Adsorption capacity q_{max} (mgg ⁻¹)	Reference
MV	Ginger Waste	10	10	1	277.7	[87]
MV	Grapefruit Peel	100	25	2.5	266.15	[88]
MV	De-Oiled Soya	10	30	0.5	95	[89]
MV	Pecan Pericarp	100	25	20	245.4	[90]
MV	Carya Illinoensis	100	12.5	1.2	463.39	[91]
MV	Gypsophila Aretioides Stem	150	4.5	5	142.97	[92]
MV	Tea Leaves	30	20	5	156	[93]
MV	Garlic Peel	100	3	3	99.9	[94]
MV	Banana Peel	50	100	32	37.41	[95]

CONCLUSIONS

Adsorption, its various types and mechanisms, adsorbents, adsorbates, and adsorption research on MV dye were all discussed in this review paper. The field of chemical engineering makes extensive use of adsorption technology for cleaning the air and water. According to the reviewed studies, both batch and column adsorption tests yield remarkable findings. Modern industrial processes have resulted in a significant increase in dye pollution. Nature, garbage, and by-products are rich sources of superior adsorbents that can be easily sourced. Some of the appealing features of these materials include a high elimination percentage, greater adsorption capacity, and improved regeneration ability. This means that the search for inexpensive adsorbents that provide superior adsorption capabilities must continue. The adsorbent was developed by recycling agricultural byproducts, however, its production and purification present significant challenges. We analyzed the progress made by various agro-waste adsorbents for use with pollutants in recent years. A variety of inexpensive adsorbents that can be made from

agricultural waste have been reviewed in this review. These biosorbents have a high affinity for dyes and can be used since they are cheap (or even free), abundant, renewable, and versatile. The efficacy of an adsorbent in removing pollutants from a solution in batch mode is affected by a number of experimental parameters including pH and dye concentration, adsorbent dosage, contact time, and adsorbent quantity. Furthermore, the column adsorption system's bed height, flow rate, and incoming dye concentration. Those who are unfamiliar with the adsorption process will benefit from this review's context and recommendations.

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