CHAPTER-2

Materials and Methodology

Chapter 2: Materials and Methodology:

This chapter has discussed and explained the materials used in the synthesis of adsorbents, the synthesis methodology that uses various characterization techniques, and the principles of researching the various adsorption removal steps during wastewater dye removal. In this chapter, the methodology's utilization of the precursors, synthesis, characterization, and removal procedures will be highlighted.

2.1. Chemicals and Apparatus:

In this scenario, what types of chemicals and apparatus are required, with source and purity. The precursor source of adsorbents, chemical reagents, with de-ionised water are used for the synthesis. Chemical and their source with purity are given in **Table 2-1**.

Chemicals	Source	Purity	Objectives
Crystal violet dye ($C_{25}H_{30}N_3Cl$)	Thermo Fisher Scientific India Pvt. Ltd.	99.99 %	For the removal study
$ZnCl_2$	Merck Ltd., Mumbai	98 %	As a chemical activating agent
$AlNO_3.9H_2O$	Titan Bio. Ltd., extra pure, India	99 %	As a precursor in the synthesis of gamma-alumina
Urea (NH_2CONH_2)	Merck Company	99 %	As a fuel source in gamma-alumina synthesis
HCl (liquid) and NaOH pellets	Merck Company	35 %	Used during washing, refluxing and pH adjustment
Na_3AsO_4	Sigma Aldrich	98 %	For an interference study
$MgCl_2$	Sigma Aldrich	99.99 %	For an interference study
$CaCl_2$	Sigma Aldrich	99.99 %	For an interference study
$FeCl_3$	Sigma Aldrich	99.99 %	For an interference study
Chromium (III) nitrate. $9H_2O$	Sigma Aldrich	98 %	For an interference study

Table 2-1 Various chemicals used with their source, purity, and utilization in dye removal.

To synthesize mesoporous carbon, biomass feedstocks were collected from the local market and agricultural fields. A solution of dye stock was prepared in a conical flask in de-ionised water and kept in the dark before the removal study. Similarly, the chemical used in the removal study of another dye is the following chemical utilized mentioned in Table 2-2.

Chemicals	Source	Purity	Objectives
Orange G ($C_{16}H_{10}N_2Na_2O_7$)	Merck India Pvt. Ltd.	99.99 %	For the removal study
Rhodamine B ($C_{28}H_{31}ClN_2O_3$)	TCI (Tokyo Chemical Industries)	98 %	For the removal study
H_3PO_4	Merck India Pvt. Ltd.	98%	As a chemical agent in mesoporous carbon synthesis
HCl (liquid) and KOH pellets	Merck Company	35 %	Used during washing, refluxing and pH adjustment
C_2H_5OH	Shri Maruti Chem. Enterprise. India	99.9%	During the regeneration study

Table 2-2. Various chemicals used with their source, purity, and utilization in dye removal.

The dye's absorbance was measured using a UV-Vis spectrophotometer (UV-1800 Shimadzu Japan), and quartz cuvettes were used for analysis. The maximum wavelengths of measurement for crystal violet, orange G, and rhodamine B dyes are 590, 488, and 554 nm, respectively. A reagent bottle of borosil brand of 60 mL is always utilized for shaking purposes in the adsorption removal study.

2.2. Preparation of Adsorbents: (Methodology)

2.2.1. Collection of Biomass:

The biomass was collected separately for preparing the adsorbent from Varanasi. Teak sawdust (from Tectona grandis tree) was collected from Chittupur gate near IIT BHU, and Corn Husk biomass was collected from the BHU agricultural field during the season. Collected sawdust and corn husk biomass were washed with 2 litres of deionised water several times and dried for 1 day at 60 degrees Celsius. The dried sawdust material was converted into fine powder and sieved through a 200 mesh, and the corn husk was ground into fine pieces for further utilization. The variability of the feedstock at different places will be different in the context of compositions, physical structure, and chemical properties. So, feedstock characterization, process optimization, and consistency and reproducibility should be utilized during the preparation of mesoporous carbon.

2.2.2. Synthesis of Adsorbent MAC and BAC

Both adsorbents were successfully converted into mesoporous and bare activated carbon using chemical and normal physical method approaches, which are illustrated in detail.

2.2.2.1. Chemical Method of Synthesis:

These approaches generally utilize a chemical activating agent as an acid, base or neutral or metal salt species to modify the surface of biomass precursor before or after the activation step of adsorbents. In case of acidic modification, HCl, H_2SO_4, H_3PO_4, and HNO_3. In case of base or metal salts, KOH, $ZnCl_2$, $CaCl_2$, NaOH, and $FeCl_3$ were utilized. Chemical modification is mostly used to alter the surface's acidity or basicity and add surface functional groups to create special qualities for eliminating dyes and inorganic substances. It was found in the literature that when KOH is used as a chemical activating agent, the form of carbon is highly microscopic. When treated with zinc chloride in a higher ratio, it gets mesopore range formation; similarly, activating with phosphoric acid, it gets changed into both micro and mesopore range of carbon [95]. So, to obtain a mesoporous carbon utilizing less costly salt, like zinc chloride, is found to be effective [96]. The detailed experimental procedure for the synthesis of mesoporous carbon from teak sawdust and corn-husk is provided as follows:

In the case of tectona grandis sawdust, the mesoporous carbon is produced using zinc chloride chemical treatment. For this approach, 15 g of sawdust is washed with de-ionised water and dried at 60 °C in a hot air oven for 12 hours. Now the dried sawdust is refluxed using HCl (1M) aqueous solution at 90 °C for 2 hours for proper breakdown of acid-degraded product in sawdust, which is cooled to room temperature and washed with de-ionised water several times to neutralize the pH. Neutralized sawdust is further dried at 60 °C in a hot air oven for 6 hours. The 15 g of sawdust is mixed with zinc chloride salts in a ratio of 1:3 in deionised water and stirred on a magnetic stirrer at 80 °C for 1 hour. The solution was stirred after the course of stirring kept cool, and stirring happened for 5 hours extra at room temperature. Further, the stirred solution is dried in an oven at 60 °C for 12 hours. This dried powder is carbonized in a tubular furnace in a nitrogen atmosphere at 550 °C for 2 hours at a ramp rate of 5 °C/min. The obtained carbon is not fully activated due so it is refluxed with HCl (1M) solution at 90 °C for 2 hours with stirring to remove the zinc chloride from carbonized carbon. Now, the solution after the course of reflux is washed several times with de-ionised water to neutralize. The carbonized refluxed carbon is dried again in a hot air oven to remove moisture, and further it is activated in an alumina crucible at 700 °C for 1 hour at a ramp rate of 3 °C/min in N_2 atmosphere. After this course of activation, the adsorbent is termed as Mesoporous Activated Carbon (MAC).

Similarly, to synthesize bare activated carbon (BAC) physical approach is utilized at the same temperature. In this, 15 g of powder sawdust is refluxed with 1 molar HCl at 90 °C for 2 hours and neutralized by deionised water washing. The powder is dried in a hot air oven at 60 °C overnight. This dried powder is carbonized in a tubular furnace at 550 °C in a nitrogen atmosphere at 5 °C/min ramp rate for 2 hours. The Carbonized carbon is taken out from the furnace and washed with de-ionised water and dried in a hot air oven. This dried carbon is activated at 700 °C for 1 hour at a 3 °C/min ramp rate in a nitrogen-based tubular furnace. This is termed as BAC (Bare-activated carbon). These adsorbents are synthesized together to check the crystal violet removal from wastewater in the laboratory. The yield of synthesized MAC and BAC adsorbent was found to be around 48% and 45 % after weighing the initial and final weights before and after synthesis. Only removal of crystal violet was performed using these adsorbents because it is the most well understood, ease of analysis, toxicity, and widespread usability in field of textiles, printing, and in biology.

2.2.2.2. Solution-Combustion Method for Gamma-Alumina Synthesis:

An aqueous solution of the fuel and oxidiser that is sufficiently exothermic to sustain a self-sustaining chemical reaction can be used to carry out Solution combustion synthesis. Generally, urea, glycine, and citric acid types of compounds are used as a fuel source during combustion steps in an aqueous medium with an oxidiser like metal nitrates. Notably, the fuel's function extends beyond simply supplying enough heat for the system; it also makes sure that stable complexes are formed with the metal ions to improve their solubility and stop the metal ions from precipitating selectively when water is removed. It is an exothermic type of reaction; when it happens, the stability of the product increases with temperature, which leads to the finalisation of the reaction. During slow cooling of the reaction, completion leads to equilibrium of the reaction, and rapid cooling puts it in a non-equilibrium state with a metastable phase [97]. To synthesize gamma-alumina, aluminium nitrate nonahydrate is generally taken, 75 grams, with urea NH_2CONH_2 from a previously reported method [98]. This aluminium nitrate is dissolved in 100 mL of de-ionised water. The addition of the calculated quantity of urea was done while preserving a 1:2 ratio between Al^{3+} and urea. Near the boiling point of water, the solution is vigorously mixed for 1 hour, and then the temperature is increased to 120 °C for further stirring. Now the solution is further heated to 250 °C for nitrate removal as a gas from the dried solution. When the complete gas of nitrate is evolved around 3 hours, the dried solid residue was collected and ground into fine powder particles. This powder is kept in an air muffle furnace at 550 °C for 3 hours of reaction to obtain the (γ-Al_2O_3) gamma-alumina. Due to the low cost of the precursor and the minimal pollution produced, this process of synthesizing gamma-alumina was simpler and more cost-effective. The process of solution combustion synthesis is an easy, quick, and energy-efficient way to create oxides with the appropriate shape. Critical parameters like as fuel type, metal precursors, stoichiometry, and pH can be controlled to fine-tune the oxide materials ultimate properties [99].

2.2.2.3. Synthesis of MAC@Al and BAC@Al: Hydrothermal Approach

Hydrothermal is a term to uses water as a solvent during the reaction in a closed autoclave at an elevated boiling temperature of water above 1 atm pressure. In place of water, any solvent can be utilized, which will be called as solvothermal process. The solvent and solute in the

hydrothermal process can be the same or different. If the same phase, it will be called a homogenous hydrothermal approach, and if different phases, it will be called a heterogenous hydrothermal process. The major advantage of this approach is to use a control method of crystallisation and composite formation with varying properties like pH, viscosity, and critical or subcritical conditions. Various energy sources are utilized for heating the hydrothermal for reaction, such as sonar, microwave, magnetic, electrical, and mechanochemical energy sources. Various nanocomposites have been made, like activated carbon/TiO_2, ZnO/Activated carbon, and carbon nanotube/ TiO_2. The majority of these composites were created in a matter of hours at lower temperatures with the aid of organic ligands and/or the proper solvent.
In numerous domains, including biology, optics, electronics, mechanics, wastewater treatments, and catalysis, these composites hold up the promise of new uses [100] [101].

To fabricate gamma-alumina decoration on mesoporous activated carbon and bare activated carbon, the hydrothermal method is utilized in deionised water. First of all, in a small 100 mL beaker, 30 mL of deionised water is taken, then 2 grams of MAC and 1 gram of gamma-alumina powder are mixed properly at normal temperature on a magnetic stirrer for about 30 minutes for proper mixing and homogenisation. Similarly, in another 100 mL beaker for BAC, 2 g gamma-alumina and 1 g are mixed. Now, after proper homogenisation of both solutions, they were kept in two different Teflon autoclaves with stainless steel covers tightened properly with a wrench, and both the hydrothermal vessels were kept in an oven at 120 °C for 3 hours of reaction in an air oven. After completion of the reaction, it was cooled and washed with deionised water once and dried at 50 °C for 3 hours. After drying, it is named as MAC@Al and BAC@Al adsorbent composite. The prepared MAC, BAC, MAC@Al and BAC@Al adsorbents are checked and compared for the crystal violet dye removal from laboratory-prepared stock dye solutions as well as from the Ganga water made crystal violet dye solution.

2.2.3. Synthesis of CHMACs Adsorbent:

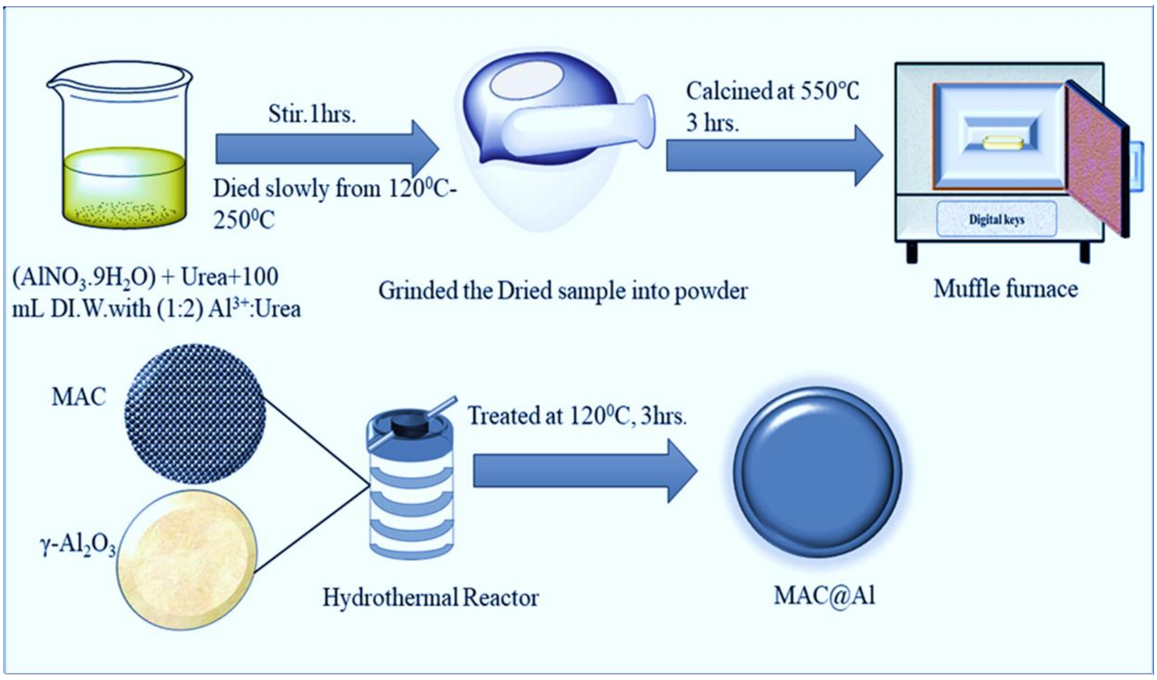
To develop a mesoporous carbon adsorbent with of high specific surface area, the chemical method of activation for biomass is forefront so far. Corn husk biomass is utilized in this section to make the high specific surface area base mesoporous activated carbon (CHMAC). For the preparation, corn husk collected from agricultural fields is washed several times and divided into small particles after grinding. The available husk was further washed with deionised water to remove impurities, dust, etc. The material was pulverised into a powder for later use after being oven-dried overnight at 60 °C. To remove any unnecessary material, 15 g of husk was refluxed at 85°C for 2 hours, washed with aqueous 1 M HCl, neutralized with deionised water, and then dried overnight at 60°C. Using different weight/weight (w/w) ratios of corn husk and orthophosphoric acid in 150 mL of deionised water, corn husk mesoporous activated carbon (CHMAC) was created.

Samples	**CHM AC 0.8 Imp 12 h**	CHMAC 0.8 Imp 7 days	CHMAC 1 Imp 12 h	CHMAC 1 Imp 7 days	CHMAC 2 Imp 12 h	CHMAC 2 Imp 7 days
H_3PO_4/CH-Powder (g/g)	4.0/5.0	4.0/5.0	5.0/5.0	5.0/5.0	10.0/5.0	10.0/5.0
Impregnation Duration	12 Hours	7 Days	12 Hours	7 Days	12 Hours	7 Days

Table 2-3. Corn husk/Orthophosphoric acid impregnation chart for CHMACs production.

On this basis, six different types of CHMACs are prepared, named as CHMAC 0.8 Imp 12 hour, CHMAC 0.8 Imp 7 days, CHMAC 1 Imp 12 hour, CHMAC 1 Imp 7 days, CHMAC 2 Imp 12 hour, and CHMAC 2 Imp 7 days. It has been synthesized using varying ratios of impregnation for 12 hours and a week. Five grams was the set biomass mass weight in grams. The density of phosphoric acid, 1.71 g/cm^3, is used to compute it. Following orthophosphoric acid impregnation, mixed corn husk was carbonized for two hours at 550 °C with a 3 °C/min ramp rate in a N_2 atmosphere. Orthophosphoric acid from carbonized carbon was removed from this material by washing it with hot water until the pH did not approach 7. To create the final CHMAC adsorbent of various orthophosphoric acid-impregnated biomass, the resulting material was activated for one hour at 700 °C at a ramp rate of 5 °C/min. The adsorption removal of orange G (OG) and rhodamine B (RhB) dye in the experiment was therefore checked by synthesizing six distinct impregnation ratio-based CHMAC adsorbents. The reaction schemes for both types of adsorbents are given in **Figures 2 (a) and (b)**, respectively.

(a)



(b)

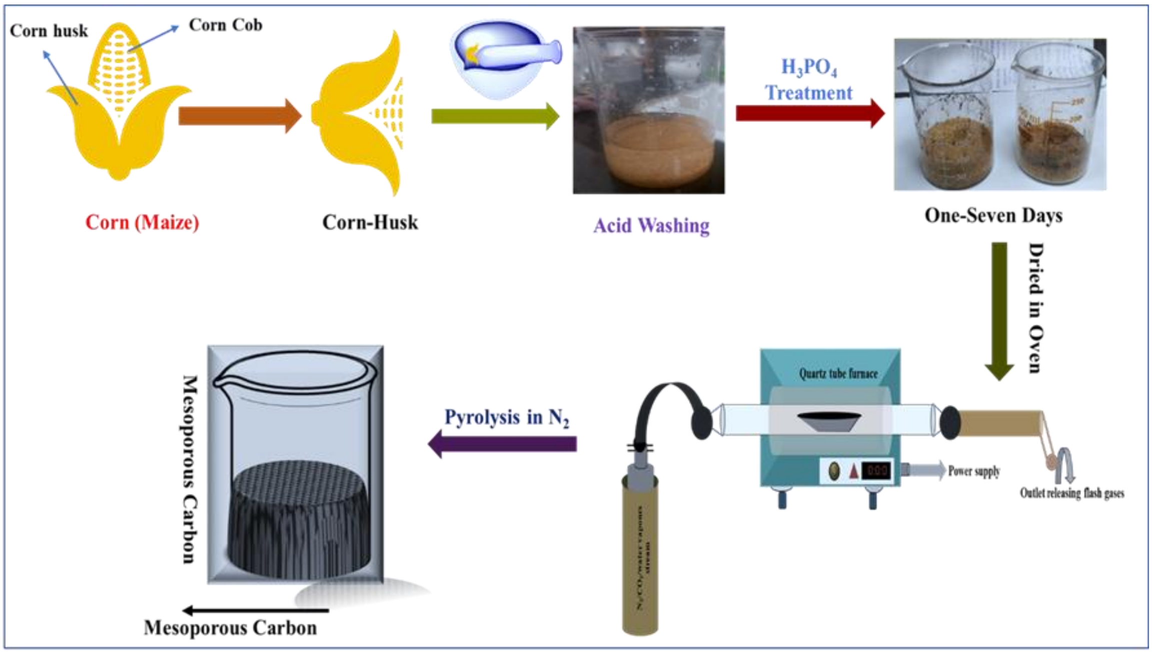


Figure 2-1. (a) Synthesis schematic for MAC@Al adsorbent **(b)** Synthesis schematic for CHMACs.

2.2.4. Adsorbents Characterization Method:

The structural characteristics, surface activity, atomic bonding, functional approach, crystallinity, elemental composition, and surface area with porosity are all defined using different characterization approaches. These are applied to the adsorbents to define the physical and chemical nature of an adsorbent. So, it is categorised into two parts, one is physical and the other is chemical characterization

2.2.4.1. Chemical Characterization:

There are numerous methods for chemically characterizing adsorbent materials that offer pertinent details about their chemical components, such as location, identification, and amount. This kind of characterization can reveal details about the functional groups that are present on the material's surface in addition to the composition of adsorbents. X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), X-ray energy dispersive spectroscopy (EDX), and ultraviolet–visible spectroscopy (UV–vis) are the chemical characterization methods most commonly used in adsorbent materials [102] [103].

2.2.4.1.1. FTIR Spectroscopy:

A method based on atom vibrations in either organic or inorganic materials is called infrared spectroscopy (IR). A material's IR spectrum can be affected by structural changes, isomorphic substitution, layer stacking order, and chemical composition. For this reason, FTIR is the most informative method for identifying various interactions between materials as well as functional groups. This method works based on a molecule being excited by infrared radiation, which causes its chemical bonds to vibrate at various frequencies in the infrared spectrum [104]. The functionality and structure of the adsorbent in which a particular bond exists determine the wavenumbers and morphologies (strong/weak; broad/sharp) of the FTIR absorption peaks associated with bending and stretching of that bond. The literature contains a variety of references that provide details on the FTIR wavenumbers associated with particular bonds. Stretching by C-H bond (2600-3000 cm^{-1}), O-H (2500-15750 cm^{-1}), C=O (1560-1815 cm^{-1}), C-O (900-1400 cm^{-1}), N-H (2800-3500 cm^{-1}), and S-H stretching (2550-2600 cm^{-1}), O-H bending (1160-1440 cm^{-1}), C-H bending (1280-1465; 1650-2000 cm^{-1}), and N-H bending vibrations (1400-1660 cm^{-1}) are the most common [105–108]. All these functionalities will be used for reference in mesoporous carbon characterization as well as in gamma-alumina. Spectrometer (Nicolet iS5, Thermo Scientific Instruments) was employed for characterization study of adsorbents.

2.2.4.1.2. X-ray photoelectron spectroscopy:

This surface-sensitive technique aids in identifying the atoms and functional groups that are present on a solid sample's surface. A photon source in the XPS apparatus shoots X-rays in the direction of the sample at high enough energy to extract electrons from atoms on the analyte's surface. A hemispherical analyzer captures these electrons and determines their kinetic energy and quantity of electrons (intensity). The intensity of the kinetic energy, which is proportional to the quantity of a particular atom or functional group present on the material under study, is connected to the electron's binding energy and gives information on the surface's chemical makeup. In the XPS graph, the x-axes cover the binding energy in electron volts, and the y-axis is all about the intensity in arbitrary units [109]. In the case of mesoporous carbon, it is used to differentiate between C-C, C-O or Al-O-Al bonds in MAC@Al and CHMACs adsorbents. XPS spectral lines are defined by the shells like 1s, 2s, and 2p, etc. From these shells ejection of electrons takes place. The chemical makeup of the surface of adsorbent materials can be described using XPS, which aids in the assessment of various synthesis and functionalization procedures and the description of an adsorbent saturated with the adsorbate [110,111]. Model K-alpha of Thermo Fisher Scientific instruments were used for analysis.

2.2.4.1.3. Raman Spectrum Analysis:

This spectroscopic technique is just the opposite of FTIR analysis; in this case, vibration of molecules takes place in the presence of visible light with the inelastic scattering principle. The techniques have a common wavelength range for detection: 532 nm, 785 nm, 835 nm, and 1064 nm. In the case of carbon types of compound analysis, three different types of specific peaks are observed, called D, G, and 2D bands. A D band comes around 1320-1380 cm^{-1}, defining the disordered hexagonal form with sp^3 hybridization. G band is an ordered form of graphitic types of hexagonal structures, with sp^2 peaks coming around 1580-1620 cm^{-1}. The 2D peak in the spectrum defines second-order (two-photon) bands between 2650 and 2750 cm^{-1}. In carbonaceous materials, the relative intensity of these two peaks, $I_{(D)}/I_{(G)}$, is frequently used to measure the disorder degree; a greater index denotes higher disorder. Raman spectroscopy is another method that can be used to confirm and assess the modification because, typically, alterations on carbonaceous adsorbents tend to decrease the bands in the spectra and/or increase the amount of disorder in the material [112–114]. Raman α-300, AFM SNOM spectrophotometer was employed in the analysis.

2.2.4.1.4. Energy Dispersive X-ray Analysis (EDAX):

The method used for elemental compositions and mapping of solid material, sometimes called EDS, EDAX or EDX. The principle behind the detection is that concentrated X-rays produced by an electron cannon excite the material. Certain electrons at lower energy levels of the atoms are removed when some of the accelerated electrons from the beam clash with them. As a result, a higher energy electron takes the place of the deleted electron and releases energy in the form of X-rays. A detector that measures the emitted energy can provide details about this particular atom. In this approach, different elements excite at a specific wavelength, making it easier to identify and quantify element amounts, measured by intensity [115]. To determine the percentage of each element on the sample's surface, EDX is frequently carried out in conjunction with SEM/FESEM analysis in adsorbent materials. It is useful for characterizing the adsorbent material, confirming successful chemical modifications, verifying the presence of the adsorbate on its surface, and evaluating changes following cycles of adsorption and desorption. Since many adsorbents are carbon-based, their composition as determined by EDX shows a majority of C, followed by O. Depending on the precursors employed in their manufacture, inorganic adsorbents can be made up of a wide range of elements, including O, N, S, Si, Fe, Mg, Al, Ti, and Ca [116–121]. The adsorbent material elements, such as aluminium, carbon, and oxygen, are experimentally determined and calculated for the MAC@Al and CHMAC adsorbents. EDS:51N1000 – EDS System was utilized for adsorbent analysis.

2.2.4.1.5. UV-Visible Spectroscopy:

This method is used for the residual concentration analysis as well as for the quality of peaks at a wavelength, so it can be used for qualitative and quantitative analysis. The principle of analysis is based on Beer's-Lambert law. Various transitions can also be obtained through this method of analysis, like the electronic transition of a molecule to molecule. Single, double and multiple bonds characteristics peaks can be analysed. A quartz cuvette, which does not absorb UV-Vis radiation, is used for sample analysis. The sources used for UV light are a Deuterium lamp, and for both UV-Vis, xenon arc lamps, and tungsten halogen lamps are used. The general wavelength range of UV-Vis is 200-800 nm. In the analysis of concentration before and after adsorption of crystal violet, orange G, and rhodamine B dye, it is applied. The standard medium of liquid for analysis was deionised water throughout the whole analysis. To calculate the removal percentage and quantity adsorbed, means adsorption capacity is calculated using the given equations.

$$\mathbf{R} = \frac{C_0 - C_t}{C_0} \times \mathbf{100} \quad \textbf{(1)}$$

And,

$$\mathbf{q_e} = \frac{C_0 - C_e}{m} \times \mathbf{V} \quad \textbf{(2)}$$

2.2.4.2. Physical Characterization:

Among the most crucial physical characteristics to take into account when assessing an adsorbent material are its size, shape, topography, surface area, magnetic characteristics, and structure. BET (Brunauer-Emmett-Teller) analysis, transmission electron microscopy (TEM), scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), and X-ray diffraction analysis (XRD) can all be used to conduct these investigations.

2.2.4.2.1. X-ray Diffraction Analysis:

This method of analysis is the basis of a synthetic adsorbent or catalyst to explain the crystallinity and amorphousness on the basis of Bragg's principle of crystal lattice analysis.

$$n\lambda = 2d\sin\theta \quad \ldots\ldots \quad (3)$$

n is the order of reflection, lambda is the wavelength of X-ray (1.54 Å), theta is the Bragg's diffraction angle, and d is the distance between the atomic planes.

During the analysis of the phase of adsorbents, the particles should be dried completely; otherwise, in the XRD instrument, it will show noise of an unwanted peak due to moisture. When a high-voltage current is supplied to the cathode filament, a speedy electron goes to the target material (anode) made up of tungsten or molybdenum, causing it to decelerate suddenly and release energy in the form of electromagnetic radiation from that anode source, known as X-rays. Generally, the X-ray diffraction for analysis of samples is divided into two categorised based on phase: one is powder XRD and another is single crystal XRD [122]. Interplanar spacing after analysis can be calculated for the samples with the average crystallite size calculation using Debye Debye-Scherrer equation. The graph of XRD is known as a diffractogram, which is drawn between 2θ vs intensity of diffraction using (Rigaku Miniflex Cu Kα radiation of 30mA and 40kV) after constructive interference of light by the planes of the crystal lattice. MAC@Al, with all co-adsorbents and CHMACs, all adsorbents have been confirmed by XRD. Miller indices obtained from XRD for each sample described the formation of the structure inside the material for further study [123–125].

2.2.4.2.2. BET Analysis:

Brunauer-Emmett-Teller in 1938 developed a method for studying adsorption mechanisms and was able to explain the multilayer phenomenon of adsorption onto the adsorbent surfaces. This method is used for the adsorbent specific surface area analysis, with various other physical properties. Generally, a gas which does not react (mostly nitrogen) with the adsorbent is taken during the analysis. the temperature is kept at 77 K, with varying pressure from 0 to 1, the volume of gas begins to be adsorbed on the surface of the adsorbent. It is an expansion of Langmuir adsorption theory. The following equation is used for the isotherm analysis of the adsorbent given as:

$$\frac{P}{V\,(P^0-P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C}\,\frac{P}{P^0} \quad \textbf{(4)}$$

As the material absorbs the gas molecules, they first cover the micropores, then the mesopores, and finally the macropores, and ultimately the entire sample surface in a monolayer of molecules. Additionally, when the gas pressure rises, new molecular layers may arise. Both the reverse process (desorption) and the amount of gas adsorbed as a function of pressure can be monitored [126]. The schematic representation of the BET adsorption process is illustrated in **Figure 2-2** below.

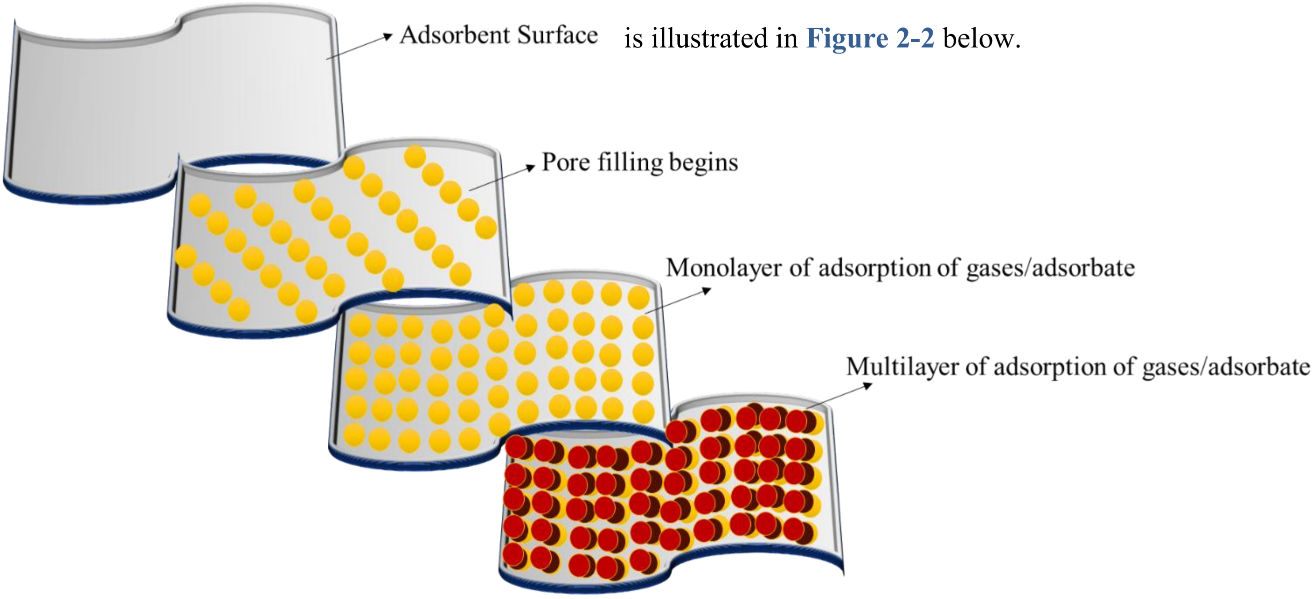


Figure 2-2. Schematics of BET analysis during pore filling of adsorbent by adsorbate (gas/liquid)

In addition to estimating the material's specific surface area, pore volume, and area, the BET model and other derived models like the Barrett-Joyner-Halenda (BJH) and Dollimore-Heal models can also determine the material's pore size distribution [127]. Furthermore, materials are categorised into six groups by the International Union of Pure and Applied Chemistry, according to the gas adsorption and desorption isotherms: Isotherm types I, II, and III show poor adsorbent-adsorbate interactions, micropores (< 2.5 nm), and the absence of micropores, respectively. Isotherm type IV identifies mesopores (2–50 nm) and capillary condensation, isotherm type V identifies weak adsorbent-adsorbate interactions and capillary condensation, and isotherm type VI identifies layer formation on a homogenous, nonporous surface [128]. Particle size, porosity, surface energy, and material homogeneity are all basic physical characteristics that are closely correlated with specific surface area. BET analysis is frequently used via Quantachrome® Asi Qwin™- Automated Gas Sorption Data Acquisition and Reduction © 1994-2013 (Quantachrome Instruments version 3.0) to assess porous adsorbents, such as carbonaceous materials, porous minerals, and polymers, since surface area and porosity have a significant impact on the loading amount of dye [129–131]. The adsorbents MAC@Al and CHMACs, specific surface area and pore size were determined using the BET and BJH methods before adsorption.

2.2.4.2.3. FE-SEM/SEM Analysis:

It is a widely used analysis for the surface topography of adsorbents to define the nature of the surface morphology, orientation of particles, variation in composition, and other phase analysis. The process entails exciting the sample with an electron beam produced by an electron cannon and passing it through a series of electromagnetic lenses within a vacuum chamber. Secondary electrons released when the beam strikes the sample are picked up by detectors, which then translate the data into a scanning image. An ultrathin layer of a conductive metal, usually gold, is applied on nonconductive samples to improve the signal

[132133]. One of the most popular characterization methods is SEM/FESEM, which may be used to show an image of a specific adsorbent material and examine its characteristics or to show how its structure has changed as a result of chemical or physical treatments or surface functionalization or decoration. Additionally, some studies have used SEM/FESEM to see how saturated the target adsorbate is with the adsorbents' surface and pores [134,135]. When we activate the adsorbent chemically, it forms a porous surface on the adsorbent, like a honeycomb structure. The rate of heating in a nitrogen atmosphere with chemical activation changed the surface topography of the adsorbent. Using a fixed potential voltage, the SEM analysis identified the surface topography of MAC@Al and CHMACs [136]. SEM; Carl Zeiss Microscopy Ltd. of Oxford Instruments Nanoanalysis was utilized for characterizations of adsorbents before and after adsorption.

2.2.4.2.4. TEM Analysis:

TEM can provide details about the shape, thickness, and approximate sizes of particles in addition to analyzing the chemical and electrical structures of materials and identifying flaws like vacancies and dislocations [137]. A uniform current-density electron beam is directed towards an ultrathin sample in conventional TEM equipment. A set of lenses that allows for variation in the sample's illuminated area is crossed by the beam. A lens system is used to image the dispersed electrons behind the irradiation sample, which experiences various forms of scattering depending on the material [138,139]. The sample preparation in TEM uses by carbon or copper grid of a specified mesh size for different types of particles. The sample is dispersed or dissolved in a solvent like water, ethanol or ethanol and sonicated to dissolve or disperse further. It is then injected into the grid and dried in an oven for the instrumental TEM analysis. The image is taken by lenses from the detector can show different particle shapes or agglomeration of particles. The material's surface area and adsorption capacity are closely correlated with the thickness and number of layers, which can be inferred from TEM pictures. High-resolution transmission electron microscopy can also be used to acquire information such as the interplanar distance and enhanced TEM images of a material's lattice structure

[140,141]. Image J software is generally used for the planes and particle size analysis of the adsorbent on a particular resolution of particles. TEM examination can be used to examine the size of the particles and other surface characteristics of adsorbents, including mineral-based nano adsorbents, carbonaceous materials adorned with metals, nano composites, and polymeric adsorbents. Fast-moving electrons with shorter wavelengths create high-quality photographs that reveal more about a material. To investigate and gather data regarding the size, shape, texture, and structure of the synthesized metal-doped or composite adsorbents for dye removal, numerous studies have used TEM in conjunction with an energy-dispersive X-ray spectroscopy detector [142].

2.2.5. Adsorption Removal Methodology:

The removal of dyes through adsorption can be accomplished in two ways: batch mode adsorption and spontaneous column mode adsorption. The adsorption process can be verified by a variety of techniques, including Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin isotherm analysis [143,144]. For batch-mode elimination, different stocks of crystal violet, rhodamine B, and orange G (500–250 ppm) were serially diluted to lower concentrations. Beer's Lambert law equation was used to calculate the dyes' residual concentrations by measuring the after-adsorption concentration of these dyes using a calibration plot [145]. The removal percentage and capacity are calculated using equations (1) and (2), respectively. Various Kinetics are also employed to check the reaction order followed by the adsorption like, Pseudo-first-order, Pseudo-second-order, Elovich model, and diffusion model, etc. All these isotherms and kinetics are defined separately in detail for adsorption purposes sequentially. For results reliability, non-linear isotherms are preferred over linear regression analysis due to the uniform distribution of errors. Both Freundlich and Langmuir are the most commonly used models to describe the adsorption isotherms. There can be no more than one adsorbate molecule per adsorbent site [146]. The isotherm and kinetics are discussed below.

2.2.5.1. Langmuir Adsorption Isotherm:

This is the first adsorption isotherm proposed by Irving Langmuir in 1916, which explains the surface homogeneity adsorption of gas molecules on the surface of a solid material. Another assumption of this model is the reversibility of the adsorption-desorption steps [147] [148]. The equation derived by Langmuir for adsorption study is:

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \qquad \textbf{(non-linear)}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(5)}$$

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \qquad \textbf{(linear)}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(6)}$$

Where q_m is monolayer adsorption capacity in mg/g, K_L is Langmuir adsorption constant, and q_e and C_e are equilibrium adsorption capacity and concentration at time t. The non-linear plot is drawn between C_e/q_e vs C_e, and the linear plot between $1/q_e$ vs $1/C_e$ with slope and intercept q_m, K_L, and $1/K_Lq_m$, with $1/q_m$ respectively.

Various dyes have been shown to follow the Langmuir adsorption isotherm in the dye removal process, with the best-fitted value. After fitting the data, a separation factor defines the value through which the process can be said to be favourable [149].

2.2.5.2. Freundlich Adsorption Isotherm:

Herbert Freundlich initially created this concept based on experimental findings. Research on absorption on asymmetrical and multisite (heterogeneous) surfaces can use this model [150]. This isotherm's non-linear expression is:

$$q_e = K_F C_e^{b_F} \quad \textbf{(non-linear)}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(7)}$$

$$\log q_e = b_F \log c_e + \log k_F \quad \textbf{(linear)}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(8)}$$

Here, the constants for this model are b_F, the adsorption strength, and k_F, the adsorption potential.

2.2.5.3. Dubinin–Radushkevich Adsorption Isotherm:

The Dubinin-Radushkevich isotherm model links adsorption with the volume of adsorbent pores. This model considers the pore structure of the adsorbent and is used on heterogeneous surfaces. To demonstrate chemical and physical processes, the DR isotherm model is utilized [151].

$$q_e = q_m e^{-(k\epsilon^2)} \text{...} \textbf{(9)}$$

Here, $\varepsilon = RT\,(1+1/C_e)$

The maximum amount of dye that can be absorbed on the adsorbent's surface is denoted by q_m. This isotherm model's constant, K, is expressed in the unit ($mol^2/kJmol^{-1}$). ε is the isotherm model's (adsorption potential) in $kJmol^{-1}$ [152].

2.2.5.4. Temkin Adsorption Isotherm:

The Temkin model assumes adsorbent-adsorbate multilayer adsorption. Both much higher and far lower concentrations are ignored by the Temkin model. The model assumes that all molecules in the layer would experience a linear decrease in heat of adsorption with logarithmic binding energies. This isotherm can be written as follows:

$$q_e = \frac{RT}{b} \ln A_T C_e \text{ ....} \textbf{(10)}$$

In this isotherm, the values b and A_T(L/mole) correspond to the Temkin constant and the heat of sorption (joules/mole), respectively. The majority of the mesoporous activated carbon material is found to be best matched by the Langmuir and the Freundlich adsorption isotherms.

2.2.6. Kinetics Study:

The reaction rate, mass transfer and diffusion processes, and surface reactions on the adsorbent during removal are all described by adsorption kinetics. The Elovich kinetic model, Ho's pseudo-second-order model, and Lagergren's pseudo-first-order model are the three most often researched kinetic models utilized in the kinetics of adsorption processes.

2.2.6.1. Pseudo-First-Order Kinetic Model:

According to the model, the rate of change in the adsorption of adsorbate at a given reaction time is precisely proportional to the difference in the concentration and rate of removal of the adsorbate over time [153]. The model, often known as Lagergren's model, is represented by the equation below [154].

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \ldots\ldots \textbf{(11)}$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \ldots\ldots \textbf{(12)}$$

both nonlinear and linear forms are given where the kinetics' rate constant is k_1, and the amounts of dye adsorbed at equilibrium and at different times are denoted by q_e (mg/g) and qt (mg/g).

2.2.6.2. Pseudo-Second-Order Kinetic Model:

The Ho and McKay equation, often known as the pseudo-second-order model, is the one that most accurately describes the adsorption of species in solution [155] [156].Surface adsorption, which includes chemisorption, is the rate-limiting stage in this paradigm, where the removal from a solution is brought on by physicochemical interactions between the two phases [157158].

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \ldots\ldots \textbf{(13)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \ldots\ldots \textbf{(14)}$$

Pseudo-second-order rate constant k_2 is used here with the same constant as in the case of pseudo-first-order [159].

2.2.6.3. Elovich Kinetic:

The two main assumptions of the Elovich model are that the adsorbent surface is heterogeneous and the activation energy rises with adsorption time. The Elovich model is an empirical model with unclear physical consequences [160]. This method is often used to model the chemisorption of gas onto solids. The following is the Elovich model:

$$\frac{dq_t}{dt} = \alpha\, e^{-\beta q_t} \text{ ………………………………………………………………… } \mathbf{(15)}$$

On integrating it, $q_t = \frac{1}{\beta}\ln \alpha\beta + \frac{1}{\beta} t\beta$ ……………………………………… **(16)**

Here, the initial desorption rate α is expressed in mg/g min for all tests, while the β desorption constant is expressed in g/mg.

2.2.6.4. Intraparticle Diffusion Model:

The diffusion that takes place when wastewater contaminants are adsorbed on the surface of an adsorbent is defined by Webber and Morris as the adsorption capacity at time t being directly proportional to the square root of time in minutes. Below is the intraparticle diffusion equation, which was investigated for crystal violet dye at a temperature of 298 K [161].

$$q_t = k_{diff}\, t^{0.5} + C \text{ ………………………………………………………………… } \mathbf{(17)}$$

where the model parameters are C (mg/g), k_{diff} (mg/g·h1/2) diffusion rate constant, and q_t (mg/g) represents the adsorption capacity at time t (h).

2.2.7. Regeneration Study:

The MAC@Al and CHMAC 2 Imp 7 days are regenerated in the dye removal process several times by using acid and alcohol. In the literature, various acid-based methods are used for dye removal. This could occur when crystal violet reacts with H_2SO_4 and HCl to form complex, colourless molecules. Similarly, a colourless complex is produced when crystal violet and NaOH react. The MAC@Al catalyst underwent batch mode desorption research for one hour at 298K and 250 rpm. The catalyst was washed with deionised water and an aqueous solution of 0.1M NaOH. Using a UV-VIS spectrophotometer, the concentration of desorbed dye was determined. Following desorption, the reusability of both dyes was evaluated by CHMAC 2 Imp. 7 days. For OG dye, 30 mL of aqueous (1M) HCl solution and 30 mL of RhB dye in a C_2H_5OH: H_2O (1:1) ratio were employed in the literature. Ultra-bath sonication was employed for 60 minutes of desorption in a water bath shaker. The adsorbent mass was around 50 mg, and it was reused for elimination by desorption for up to seven cycles. The adsorption process was examined using a 60 mL dye solution volume and a 60 mg/L concentration of dye. The UV-vis spectrophotometer was used to analyze the residual concentration following each adsorption and desorption of both dyes. The desorption efficiency or regeneration percentage removal of dyes is calculated by using the following equation [162,163,164].

$$(\%)\ \text{Desorption efficiency} = \frac{\text{Desorbed dye concentration in mg/L}}{\text{Adsorbed dye concentration in mg/L}} \times 100 \quad \ldots\ldots\ldots\ldots \quad \mathbf{(18)}$$

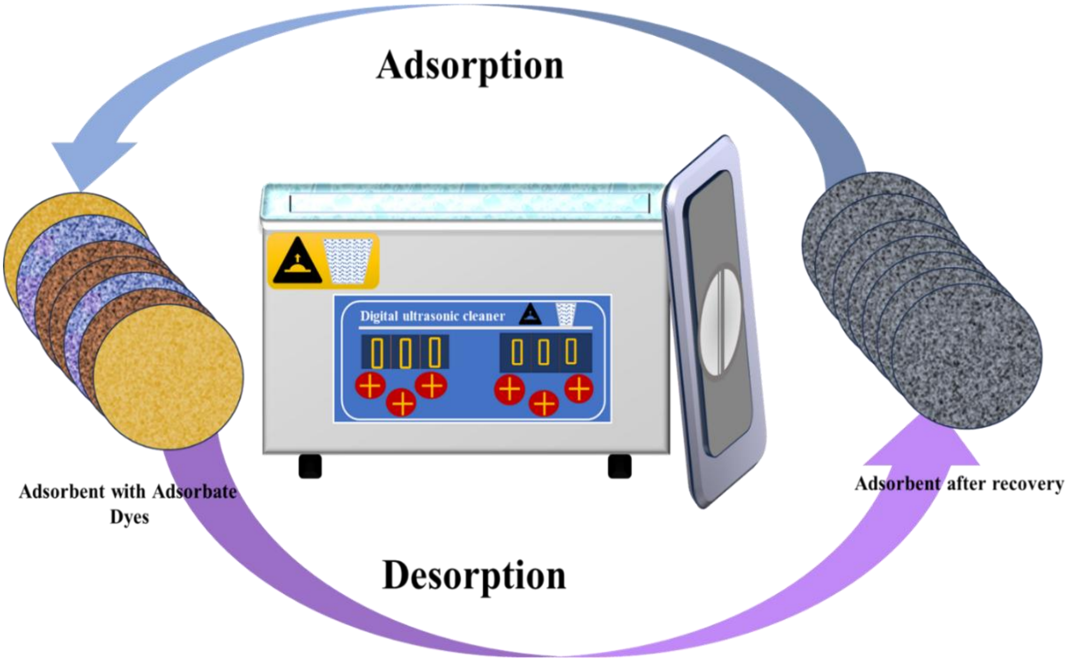


Figure 2-3 Schematics of the desorption process with the use of water bath sonication.