CHAPTER 2

Materials and methods

2.1 INTRODUCTION

This chapter provides a comprehensive outline of the experimental process for batch systems. It also presents an introduction to different techniques used for characterization, including Scanning Electron Microscopy analysis, Fourier Transform-Infrared spectroscopy, Zeta potential measurement, X-Ray Photoelectron Spectroscopy, Energy-Dispersive X-Ray Spectroscopy, X-ray diffraction analysis, and Brunauer-Emmett-Teller method. Furthermore, it explores various isotherm models such as Langmuir and Freundlich, along with their key parameters in great detail. Additionally, several commonly utilized kinetic models are written about and applied to the experimental data within this segment of the thesis.

2.2 MATERIALS

The chemicals utilized in the synthesis process and adsorption experiments are all of analytical grade and were used without any additional purification. The reagents and chemicals employed in the experimental procedures are detailed in Table 2.1 and Table 2.2. Throughout this study, deionized water was used consistently for all the experiments. To prepare a stock solution of fluoride ion at a concentration of 1000 mg/L, 221 mg of NaF was dissolved in 1000 mL of water, with other test solutions subsequently prepared through dilution from the stock solution. Similarly, a standard stock solution of nitrate ion at a strength of 100 mg/L was created by dissolving 360.9 mg of potassium nitrate into 500 mL DW water; different concentrations for adsorption experiments were then obtained through subsequent dilutions from this stock solution.

Table 2.1 List summarizing all chemicals and feedstocks used throughout the study

S.No	Chemical name	Chemical formula	Molecular weight (g/mol)	Physical appearance	Manufacturer
1	Sodium fluoride salt	NaF	41.99	White/solid	Sigma-Aldrich
2	Hydrochloric acid	HCl	36.46	Colourless/Liquid	SD Fine
3	Sodium hydroxide	NaOH	40	White/Pellets	Qualigens
4	Ammonium Cerium (IV) Nitrate	$(NH_4)_2Ce(NO_3)_6$	548.22	Yellow/solid	Sigma-Aldrich
5	Ammonium hydroxide	NH_4OH	35.05	Colourless/Liquid	Qualigens
6	Potassium nitrate	KNO_3	101.10	White/solid	Sigma-Aldrich
7	Deionized water	H_2O	18.02	Colourless/Liquid	-
8	Potassium hydroxide	KOH	56.10	white or slightly yellow	Sigma-Aldrich
9	Hydrogen peroxide	H_2O_2	34.01	colorless liquid	Sigma-Aldrich

Table 2.2 Other Feedstocks used throughout the study

S.No	Material name	Source	Treatment/Preparation
1	Sugarcane bagasse	Juice shop, IIT BHU	Cleaned, sun-dried, milled, and sieved
2	Naked corn cobs	Kitchen waste	Milled, sieved, and oven-dried (80 °C)
3	Electric Geyser Waste scale build-up	IIT BHU hostel	Collected during geyser cleaning

Fig 2.1: Biomass feedstock for biochar production and EGWS (Scaling waste)

2.3 SYNTHESIS OF BIOCHAR'S

Sugarcane bagasse was obtained from a juice shop on the campus of IIT BHU, Varanasi. It underwent thorough cleaning with tap water and de-ionized water before being sun-dried until its weight remained constant. The dried bagasse was then ground into powder using an electric grinder and sieved to obtain a fine powder with particles smaller than 0.149 mm size. This powdered material was pyrolyzed in a tube furnace at 600 °C for 2 hours under an inert atmosphere, where pure N_2 gas was circulated through the furnace to maintain the environment. The resulting biochar was cleaned with deionized water, then dried at 80 °C in a hot air oven after which it underwent treatment by immersion in 0.1 M HCl overnight to remove any soluble ash content. This raw bagasse biochar is referred to as Biochar and stored in an airtight desiccator for subsequent modification purposes. Similarly, Corn cob biochar is prepared by collecting corn cobs from a kitchen waste, removing any external impurities by washing several times using de-ionized water, and drying them in the sun. Then it was processed by milling, sieving, and oven-drying at 80 ºC. Subsequently, the corn cob powder underwent pyrolysis in a tube furnace under an inert atmosphere with a slow temperature increase to 600 ºC over 2 hours. The resulting biochar was then washed with DI water and dried at 80 °C before being stored as CBC in a hermetic container for future use.

2.3.1 Precipitation method of synthesis

The precipitation method is employed for synthesis of CeO_2/BC. It involves the formation of a solid precipitate from a supersaturated solution by altering its physical or chemical conditions. The stages involve in this procedure are:

Solution Preparation: A solution containing the desired metal precursors (salts, complexes) is prepared. The choice of precursor and solvent significantly influences the properties of the final adsorbent.

Precipitation: A precipitating agent (e.g., alkali hydroxide, ammonia) is added to the solution, causing the formation of insoluble metal hydroxides or other compounds. The precipitation conditions, such as pH, temperature, and concentration, are crucial in determining the particle size, morphology, and crystallinity of the precipitate.

Aging: The precipitate is often aged under specific conditions (temperature, time) to enhance its properties. Aging promotes particle growth, improves crystallinity, and reduces impurities.

Filtration and Washing: The precipitate is separated from the mother liquor by filtration and washed thoroughly to remove impurities.

Drying: The wet precipitate is dried to remove residual moisture.

2.3.2 Ball Milling method for Biochar Modification

Ball milling is a physical process that involves the reduction of particle size through repeated impact between the material and grinding media in a rotating container. This technique has been extensively applied in the modification of biochar. By subjecting biochar to ball milling, significant alterations in its physical and chemical properties can be achieved, enhancing its performance in various applications.

The modification of biochar through ball milling occurs primarily via two mechanisms:

Mechanical Fracture: The high-energy collisions between the biochar particles and the grinding media lead to the breakdown of the biochar structure, resulting in a decrease in particle size and an increase in specific surface area. This enhanced surface area provides more active sites for adsorption, catalysis, and other processes.

Surface Functionalization: Ball milling can induce the formation of new functional groups on the biochar surface. The intense mechanical forces generated during the process can break existing chemical bonds and create reactive sites. These functional groups, such as hydroxyl, carboxyl, and carbonyl groups, can significantly improve the biochar's affinity towards various compounds, including pollutants, heavy metals, and organic molecules.

Several factors influence the outcome of the ball milling process:

Grinding media: The type and size of the grinding media (e.g., steel, tungsten carbide, zirconia) affect the milling efficiency and the properties of the modified biochar.

Ball-to-biochar ratio: The ratio of the mass of grinding media to the mass of biochar influences the milling intensity and the resulting particle size distribution.

Milling time: The duration of the milling process determines the extent of particle size reduction and surface modification.

Milling atmosphere: The atmosphere in the milling chamber (e.g., air, inert gas) can affect the oxidation or reduction of the biochar surface.

2.4 CHARACTERIZATION

2.4.1 Determination of Zero-point charge (pH_{PZC}) of the adsorbent

The point of zero charge (pH_{PZC}) plays a significant role in the adsorption process in aqueous solutions. It indicates the pH level at which the surface charge on an adsorbent is neutral, and it greatly aids in characterizing metal oxides and hydroxides. The pH_{PZC} also determines a substrate's ability to adsorb ions from a solution during the adsorption. The pH_{PZC} was determined using the salt addition method, as detailed by Srivastava et al. (2011) and Farooq et al. (2012) [148,149]. This involved preparing an aqueous solution of 0.01M NaCl and adjusting its pH from 3 to 12 at one-unit intervals using 0·01 M HCl and NaOH solutions. Next, 30 mg of adsorbent is added to flasks containing 10 ml of 0.01 M NaCl solutions at varying pH levels. Then the solutions are agitated on an orbital shaker at 150 rpm for 24 hours at controlled temperature. The final step involves filtering each solution and recording their respective final pH values. After plotting a graph of the initial pH against ΔpH (the difference between the solution's initial pH and final pH) values, we can determine the pH_{PZC} of the adsorbent at the point where $pH_f - pH_i$ equals 0.

2.4.2 Thermogravimetric analysis (TGA)

Thermogravimetric analysis is a technique used to study the thermal behavior of materials. Thermogravimetric analysis is a thermal analytical method used to examine the variation in physical and chemical properties of a material change as temperature increases, from room temperature to the maximum set on the instrument. This technique was employed to analyze the thermal stability of the adsorbent material. TGA can be used to investigate both physical changes, such as vaporization, melting, crystallization, and volume change by expansion and contraction, as well as chemical changes like the formation of new products, oxidation, decomposition, chemisorption, corrosion and dehydration. Thermogravimetric analysis involves monitoring the sample's mass changes with temperature using a specific heating rate in a controlled atmosphere. The resulting graph showing mass loss versus temperature is called a thermogram. TGA of uncalcined samples was done using (TG/DSC/DTG) SII 6300 EXSTAR. TGA was conducted by subjecting the sample to a temperature range from 30˚C to 1000˚C at a heating rate of 10 °C/min under a nitrogen atmosphere.

2.4.3 Scanning Electron Microscopy (SEM) Analysis

SEM analysis is performed to examine the surface morphology and structure of the adsorbent. This technique allows for high-resolution imaging of the adsorbent's surface, providing valuable insights into its physical structure, porosity, and particle size distribution. The instrument used for SEM analysis of CeO_2/BC was Nova Nano SEM 450 equipped with Team Pegasus Integrated EDS-EBSD with Octane Plus and Hikari Pro and EVO Scanning Electron Microscope MA15 / 18 was used for SEM analysis of CaO@CBC. SEM analysis involves bombarding the surface of the sample with electrons and then collecting the various signals emitted from the sample. These signals are then used to create an image of the sample's surface. Additionally, SEM can provide information about the elemental composition of the sample through energy-dispersive X-ray spectroscopy analysis, which is often performed concurrently with SEM to obtain both structural and elemental information in the same analysis. During the process of SEM analysis, the sample is prepared by coating it with a thin layer of conductive material, such as gold or carbon, to prevent the accumulation of electrostatic charge on the sample.

2.4.4 Xray diffraction technique (XRD)

X-ray diffraction is a non-destructive technique used to analyze the crystalline structure of a material. It works by directing X-rays at a sample, and observing the pattern created as the X-rays are diffracted by the atoms within the crystal lattice. The resulting peaks in the XRD pattern provide information about both individual planes within the lattice and the overall arrangement of atoms in the crystal structure. XRD patterns were obtained by using a Rigaku Miniflex 600 powder diffractometer with Cu Ka monochromatic radiation at specific voltage and current settings of 45 kV and 15 mA. The XRD patterns were recorded within a specific angular range of 10 °-90 ° and scan rate 5 per minute and a step size of 0.02 °, and the resulting diffractogram was analyzed using the JCPDS database to identify and determine the crystal structure of the catalysts.

2.4.5 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy is a surface-sensitive analytical technique that provides information about the elemental composition and chemical bonding states of materials. It operates by exposing the sample to X-rays and detecting the kinetic energies of the photoelectrons that are ejected from the material's surface. These energies can be employed to determine the elemental constituents present within the sample and provide information about different oxidation states of single element [150]. X-ray photoelectron spectroscopy (XPS) was carried out by using K-Alpha (Thermo Fisher Scientific) spectrometer equipped with a monochromatic X-ray source at 1486.6 eV (Al K line).

2.4.6 Fourier-Transform Infrared (FT-IR) spectroscopy

FTIR spectroscopy is a technique that analyzes the molecular composition of a sample. It works by measuring the absorption, emission, or reflection of infrared light as it interacts with the sample. This technique offers insights into the functional groups and chemical bonding present within the sample, enabling the identification of the constituent compounds. An FT-IR spectrometer accurately separates spectral data with a high resolution of 4 cm^{-1} across a wide infrared range from 400 to 4000 cm^{-1}. The fingerprint region, spanning from 400 to 1400 cm^{-1}, is significant for representing the structure of organic or inorganic materials. Beyond 1400 cm^{-1} lies the functional group region that displays the vibrations of specific functional groups. Using Fourier Transform, the raw data (counts per seconds) is converted into an actual spectrum. In this study, synthesized samples were analyzed using Nicolet iS5 FT-IR spectrometer within the range of 500-4000 cm^{-1} by employing KBr pellets suitable for spectroscopy.

2.4.7 Brunauer-Emmett-Teller (BET) surface area analysis

BET surface area analysis is a technique used to determine the specific surface area and porosity of materials. This technique involves the adsorption of gas molecules onto the surface of the material and measuring the amount of gas adsorbed at different pressures. This allows for the calculation of the surface area and pore size distribution of the material. This research utilized the BELLSORP MAX II and BELCAT-II instruments. Prior to analysis, all samples were degassed using N_2 gas for 12 hours at 300 °C. The surface area was assessed using the Brunauer–Emmett–Teller method, while the volume and pore diameter of the synthesized samples were calculated using the BJH method.

2.5 EXPERIMENTAL PROCEDURE

2.5.1 Batch adsorption experiments

Batch adsorption studies for nitrate and fluoride were conducted to evaluate the adsorption capacity and efficiency of the synthesized adsorbents. Stock solutions of nitrate and fluoride were prepared by dissolving potassium nitrate and sodium fluoride in de-ionized water and the standard solutions of desired concentrations prepared by diluting the stock solutions. A pre-decided amount of the adsorbent was added to each adsorbate solution taken in Erlenmeyer flask. The beakers were then shaken on a mechanical thermostat shaker (NSW-133 "Super Deluxe" by Narang Scientific Works Pvt. Ltd.) for a predetermined amount of time to allow for adsorption to occur. The solution was then separated using centrifugation from the adsorbent, and the concentration of the adsorbate in the solution was measured. The impact of solution pH was investigated by adjusting the pH of the solution within the range of 2 to 12 using 0.1 M HCl and 0.1 M NaOH. Then the solution is kept for stirring at 120 rpm in mechanical thermostat shaker for pre-determined contact time and adsorbent dose.

An ion chromatography technique using Metrohm Dual Channel 930 Compact IC Flex instrument was used to measure the amount of residual fluoride and nitrate ions present in the solution. Using the following equation, the amount of adsorbate on adsorbent, qe (mg/g), was determined:

$$\boldsymbol{q_e = \frac{(C_e - C_0)V}{m}}$$

Where V (L) denotes the volume of the solution, m (g) represents the mass of the adsorbent utilised, and C_o and C_e (mg/L) means the initial and equilibrium concentrations of adsorbate in solution, respectively.

2.5.2 Adsorption kinetics models

Kinetic studies were investigated with different initial concentrations for fluoride and nitrate, while maintaining a constant adsorbent dosage and pH at 7 ± 0.3 for each with continuous shaking for fixed time duration. The samples were subjected to centrifugation, and the remaining fluoride and nitrate concentrations were determined at specified time intervals. The Lagergren pseudo-first-order (PFO) model, established in 1898, is a cornerstone kinetic model used extensively in adsorption studies [151]. This model posits that the rate of adsorption is directly governed by the availability of unoccupied sites on the adsorbent surface. Its applicability is particularly relevant during the initial adsorption stages when a high number of these active sites are present. The model assumes the rate of adsorption is directly proportional to the number of unoccupied sites on the adsorbent surface. This means that when more sites are available, the adsorption is faster. As time progresses, the number of free sites decreases, and the rate of adsorption slows down exponentially. This is reflected in the mathematical equation of the model. By fitting experimental data to the PFO model, researchers can determine constant (k_1) that indicates how quickly the adsorption process occurs. Equilibrium adsorption capacity (q_e) that represents the maximum amount of adsorbate the adsorbent can hold at a specific set of conditions.

Complementing the Lagergren pseudo-first-order model, the Pseudo-second-order (PSO) model offers another perspective on adsorption kinetics. This model proposes that the rate of adsorption is proportional to the square of the occupied sites on the adsorbent surface. This suggests a chemisorption mechanism, where electron sharing or exchange occurs between the adsorbate and the adsorbent, forming stronger bonds. The PSO model is particularly applicable during the later stages of adsorption when a significant portion of the active sites are already filled. By fitting experimental data to the PSO model, researchers can extract the rate constant (k_2) that indicates the strength of the interaction between the adsorbate and the adsorbent surface, influencing the rate of adsorption. Equilibrium adsorption capacity (q_e) that represents the maximum amount of adsorbate the adsorbent can hold under specific conditions. and predict the ultimate adsorption capacity. While also empirical, the PSO model sheds light on the mechanism of adsorption within active sites and provides valuable insights into the complete adsorption process.

The mathematical representations of these models are as follows [152]:

Pseudo first-order adsorption kinetic model:

$$\ln (q_e - q_t) = \ln q_e - k_1 t$$

Pseudo second-order adsorption kinetic model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where q_e is the amount of adsorbate (mg/g) at equilibrium, q_t is the amount of adsorbate on adsorbent (mg/g) at time t (min), k_1 is the rate constant (min^{-1}) for pseudo-first-order kinetics and k_2 is the rate constant (g/mg/min) for pseudo-second-order kinetics. The kinetics data were plotted as t/qt vs. time for the pseudo-second-order kinetics model, and k_2 values were determined from the intercept and slope of the plot.

2.5.3 Adsorption isotherms models

Adsorption isotherm studies for both fluoride and nitrate were explored by using solutions with varying concentrations, for fluoride and nitrate. Dose of adsorbent, pH and contact time were fixed. Then the quantification of residual fluoride and nitrate ions in the solution was performed. Irving Langmuir proposed the Langmuir isotherm model in 1916, and it is a key component of the theory underlying adsorption processes. It offers a foundational structure for comprehending the relationship between an adsorbent and a solute. The model rests upon a set of well-defined hypotheses [153].

Langmuir speculates a scenario limited to monolayer adsorption. This implies a finite number of well-defined binding sites on the adsorbent surface, each capable of accommodating a single adsorbate molecule. The model envisions a uniform distribution of adsorption sites with identical properties. These sites possess equivalent energetic environments, resulting in constant adsorption energy across the entire surface. This eliminates the influence of spatial heterogeneity on the adsorption process. The Langmuir model assumes no attraction or repulsion between adsorbed molecules, simplifying the analysis.

The Freundlich isotherm is another widely used empirical model for describing adsorption processes, especially for heterogeneous surfaces and multilayer adsorption. It was proposed by Herbert Freundlich in 1906 and is based on the following key characteristics [153].

The Freundlich isotherm is suitable for representing nonlinear adsorption behavior, where the adsorption capacity does not increase linearly with the concentration of the adsorbate. Unlike the Langmuir model, the Freundlich isotherm is applicable to surfaces with heterogeneity in adsorption sites. It accounts for the fact that not all adsorption sites have the same affinity for the adsorbate. The Freundlich model allows for a more flexible representation of adsorption data compared to the Langmuir model. It is particularly useful when the adsorption process involves multiple layers of adsorbate molecules on the surface of the adsorbent or when the adsorption sites have varying affinities for the adsorbate.

These models were shown as follows:

The mathematical representations of these models are as follows [154]:

Langmuir model:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{K_L q_{max}} \frac{1}{C_e}$$

The linear form of Langmuir's isotherm model is given by the following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}}$$

Freundlich model:

$$\boldsymbol{q_e = K_F C_e^{\frac{1}{n}}}$$

The linear form of Freundlich's isotherm model is given by the following equation:

$$\boldsymbol{lnq_e = lnK_F + \frac{1}{n} lnC_e}$$

Where C_e was the equilibrium concentration of adsorbate in solution, q_{max} was the maximum adsorption capacity. In these models, q_e was the amount of equilibrium per gram, and K_L (L/mg) was the Langmuir constant related to the affinity of adsorbate with the binding sites. K_F was the Freundlich isotherm constant related to adsorption capacity, n was associated with the heterogeneity of the adsorption site energies.

The Temkin isotherm is a theoretical model employed to describe the adsorption behavior of adsorbates onto a heterogeneous adsorbent surface. It posits that the heat of adsorption of all the molecules in a layer decrease linearly with coverage due to adsorbate-adsorbate interactions. This implies that the adsorption energy is not constant but rather decreases linearly with increasing coverage.

The linear form of Temkin's isotherm model is given by the following equation:

$$\boldsymbol{q_e = BlnK_T + BlnC_e}$$

Where q_e is the equilibrium adsorption amount (mg/g), B is the Temkin isotherm constant related to the heat of adsorption (J/mol), K_T is the equilibrium binding constant (L/g) and C_e is the equilibrium concentration of the adsorbate in solution (mg/L).

2.5.4 Thermodynamic studies

The thermodynamic evaluation of the adsorption process is essential as it provides insight into the Gibbs free energy change (ΔG°), which helps predict the feasibility of the adsorption process. Additionally, this evaluation allows for the determination of other parameters such as enthalpy change (ΔH°) and entropy change (ΔS°), which are crucial for understanding whether the adsorption process is endothermic or exothermic. The thermodynamic parameters can be calculated using the following equation:

$$\Delta G^{o} = -RT\ln K_0$$

$$\Delta G^{o} = \Delta H^{o} - T\,\Delta S^{o}$$

$$\ln K_0 = \frac{\Delta S^{o}}{R} - \frac{\Delta H^{o}}{RT}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (K), and K_0 is the thermodynamic equilibrium constant. K_0 can be calculated from of the linear fit of $\ln (q_e/C_e)$ to C_e.