CHAPTER 3

RESEARCH METHODOLOGY

3.1 Chemicals and Materials

Chemicals and solvents were purchased from Sigma Aldrich and Evachem. They were used as received without further purification. The list of chemicals and materials is stated in Table 3.1.

Table 3.1: List of Chemicals and Materials

Chemical	**Molecular Formula**	**Manufacturer/ Supplier**
Sodium Carboxymethyl Cellulose	NaCMC	Evachem
Sodium Hydroxide	NaOH	Sigma-Aldrich
Glycerol	$C_3H_8O_3$	Sigma-Aldrich
D- (+)-gluconic acid-lactone	GDL	Sigma-Aldrich
Magnesium (II) Chloride Hexahydrate	$MgCl_2.6H_2O$	Sigma-Aldrich
Nickel (II) Sulphate Hexahydrate	$NiSO_4.6H_2O$	Sigma-Aldrich
Manganese (II) Sulphate Monohydrate	$MnSO_4.H_2O$	Sigma-Aldrich
Zinc (II) Sulphate Heptahydrate	$ZnSO_4.7H_2O$	Sigma-Aldrich

3.2 Synthesis of Carbon Aerogel (CA)

Firstly, 4% CMC aerogels were prepared by weighing commercial grade sodium carboxymethyl cellulose (NaCMC), D-(+)-gluconic acid-lactone (GDL) and glycerol in a ratio of 8:4:1 and dissolving them in 200 mL of deionized water. The solution was stirred under magnetic stirring at room temperature for 30 minutes until a transparent solution was attained. Several metal (magnesium (Mg), manganese (Mn), nickel (Ni), zinc (Zn)) solutions with various concentrations (0.002, 0.004, 0.006, 0.008, 0.01 mol) were prepared in 5.5 mL of deionized water and 0.5 mL of 0.01M sodium hydroxide (NaOH) solution. The mixtures were then mixed with NaOH solution and stirred until a homogeneous solution was obtained.

Following that, each of the metal ions solution was mixed with the obtained CMC solution for 5 minutes to ensure homogeneity. The mixed gel solutions were then poured into a cylindrical polystyrene tubule and left at room temperature for 3 days to encourage the gelation and cross-linking reactions. Lastly, the CMC hydrogel underwent freeze-drying at -50 ℃ for 60 hours to obtain the CMC aerogels. The CMC aerogels were then turned into carbon aerogels (CA) by carbonising them in a tube furnace at 800 ℃ for 2 hours at a heating rate of 5 ℃/minutes under Nitrogen (N_2) atmosphere, as shown in Figure 3.1 (Yu et al., 2017).

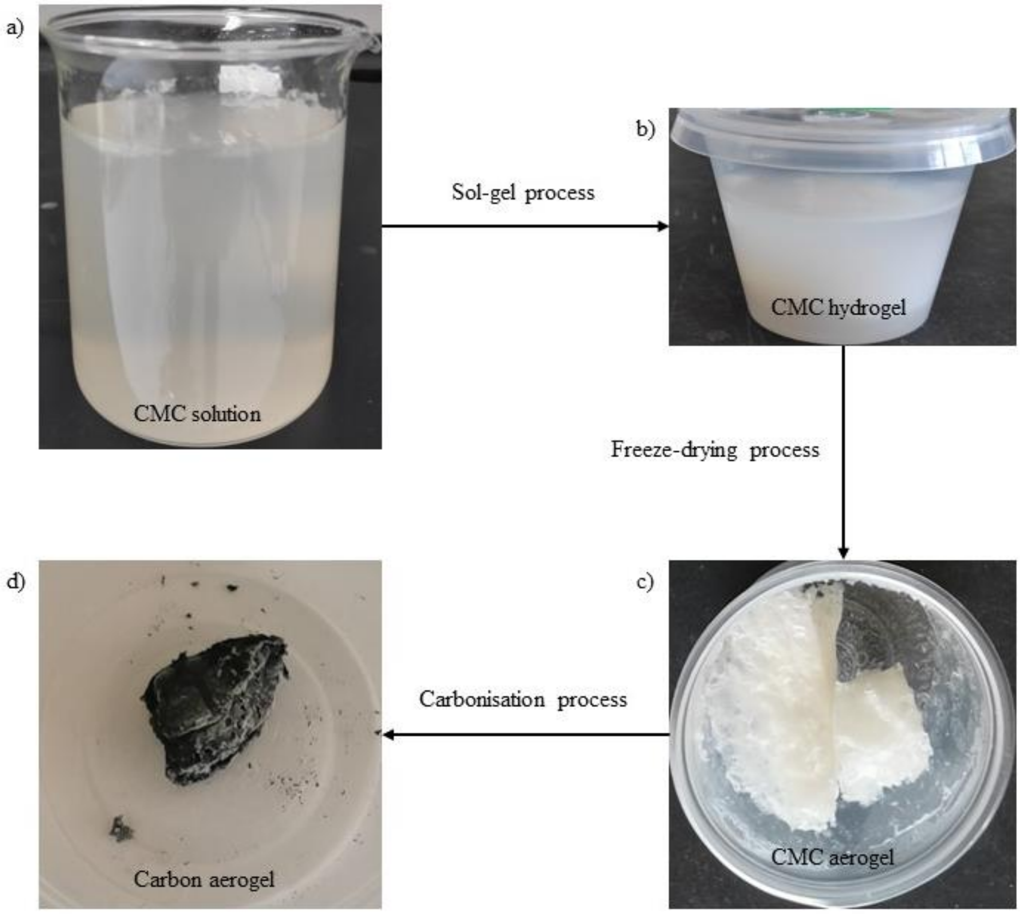


Figure 3.1: Synthesis of CA Derived from CA: a) Preparation of 4% CMC Solution. b) Sol-gel Process between CMC Solution and Metal Ions Solution to Form CMC Hydrogel. c) The CMC Hydrogel was then Freeze-dried to Obtain CMC Aerogel. d) The CMC Aerogel was Undergone Carbonisation Process to Obtain CA.

3.3 Characterisation of Carbon Aerogel (CA)

In this research, six instruments were used for characterisation of CA: FTIR spectrometer, XRD analyser, BET surface area analyser, FESEM and TPD analyser.

3.3.1 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy was used to determine the functional group and possible molecular bonds in CA before and after carbonisation. The changes were observed to determine the completion of carbonisation where most of the molecular bonds were destroyed during carbonisation (Mohamed et al., 2017). Thermo Scientific Nicolet iS50RFTIR spectrometer was used to analyse the CA sample. The FTIR was equipped with DLaTGS detector, and an automated beam splitter exchanger connected to the software of the spectrum operating system (OMNIC Software) for FTIR data collection.

The sample was placed using a spatula in direct contact with attenuated total reflectance (ATR) crystal on a multibounce plate. FTIR was recorded from 8 scans at a resolution of 4 cm^{-1} at 4000 – 400 cm^{-1}. These spectra were subtracted from the background air spectrum. After every scan, a new reference air background spectrum was taken. The ATR plate was carefully cleaned twice with methanol and dried with soft tissue before being placed with the next sample. Cleanliness was verified by collecting a background spectrum and comparing it with the previous one. These spectra were recorded as transmittance values at each data point. The FTIR spectra were observed at peak formation between 4000 cm^{-1} until 1500 cm^{-1} which represented the functional groups and molecular bonds of the sample.

3.3.2 X-Ray Diffraction (XRD) Analyser

The crystal structure of pure CA and CA crosslinked with metal ions was characterised by analysing the XRD patterns of the samples at 2θ range of 2° to 90°. These patterns revealed whether the samples were amorphous or crystalline. In addition, the presence of any metal oxide formed during the carbonisation process was observed. XRD analysis was conducted on a Rigaku model MiniFlex 600. Firstly, the sample had to be as pure as possible and in the form of a fine powder in order to be placed and fitted into the sample holder. The intensity of diffracted x-rays was continuously recorded as the sample and detector rotated through their respective angles. The results were presented as peak positions at 2θ and x-ray counts (intensity) in the form of a table or x-y plot.

3.3.3 Brunauer-Emmett-Teller (BET) Surface Area Analyser

The specific surface area and pore size of pure CA and CA crosslinked with metal ions were determined using a BET analyzer. This analysis was aimed at determining which CA samples with various concentrations have the highest surface area and pore size. CA samples that met the desired criteria were selected for further study towards the possibility of being used as hydrogen storage materials. Surface area and pore size analysis of the CA sample were carried out via the nitrogen adsorption/desorption technique using the BET surface area analyser. The analyser was equipped with two independent vacuum systems, one for sample preparation and one for analysis, where both systems could run concurrently.

The CA sample was fitted into a bulb shaped, glass sample tube holder that can hold volumes from 1 cm^3 to 20 cm^3. The mass of the sample needed was dependent on material density and expected specific surface area (SSA). It was recommended to use between 40 m^2 and 120 m^2 of total surface area per sample for the best surface area analysis results. The sample was sufficiently dried during the degas step when the evacuation rate was < 5 µmHg/min, usually in 6 to 8 hours to avoid negative interference between the sample and nitrogen gas (N_2). N_2 was used as a physisorption gas for porosity measurement. Then, the sample was backfilled with helium gas (He) and allowed to cool to room temperature. The mass of the sample and sample tube holder were weighed and subtracted from the sample holder mass recorded earlier. The data was recorded using ASAP 2020 software.

3.3.4 Field Emission Scanning Electron Microscopy (FESEM)

FESEM was used to analyse the morphology of CA crosslinked with and without metal ions at different concentrations. The surface morphology of the CA was analysed by the FESEM model JSM IT800 SHL. Prior to observation, CA was sputtered-coated with a thin layer of gold. The FESEM analysis was performed by bombarding the target surface with 1 keV electrons that had previously been spread over an aluminium stub with double-edge tape. Electrons emitted from the sample with an energy of 1 KeV were defined as secondary electrons and used for sample analysis.

3.3.5 Temperature Programmed Desorption (TPD) Analyser

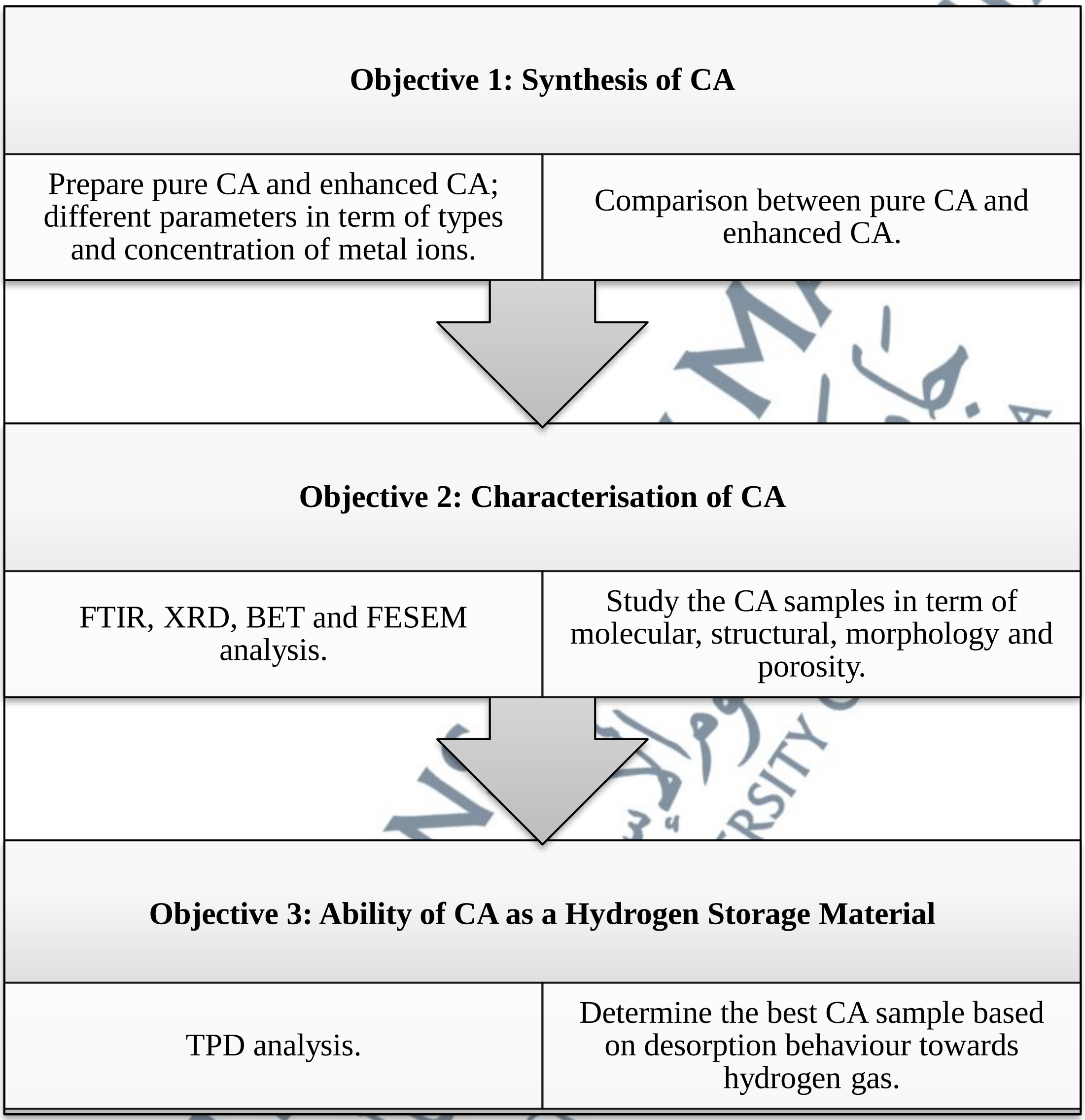
The desorption behaviours of hydrogen storage materials were studied using TPD over a wide temperature range. After crosslinking the CA sample with various metal ions, the samples' capability as hydrogen storage material was analysed. This analysis was aimed at determining how metal ions can enhance the hydrogen desorption behaviour of CA. Temperature Programmed Desorption (TPD) 1100 by Thermo Scientific was used in this analysis. The TPD analysis was started by cleaning the sample with helium gas (He) at 50 °C for 1 h (degas process). Then, the sample was pre-saturated with hydrogen gas (H_2) at 50 °C for 1 h (adsorption process). The sample needs to be purged with He again as the system temperature decreases to room temperature. The data collection began at room temperature and gradually increased to 500 °C at a ramp rate of 10 °C min^{-1} (desorption process). At a certain temperature, the bond breaking between the sample and the H_2 occurred, and the H_2 gas was desorbed. The desorbed gas entered the steam of inert carrier gas and was swept to the detector, where the detector response was proportional to the gas concentration. The TPD curve was shown on the analyser monitor.

3.4 Ability of Carbon Aerogel (CA) as a Hydrogen Storage Material

The TPD curve of CA samples from room temperature to 500 °C, which indicated the desorption behaviour of CA samples as hydrogen storage materials, was used to analyse their ability as hydrogen storage materials. Firstly, CA samples were degassed with helium gas (He) at 300 °C for 60 min to remove any unnecessary materials. Then, the temperature was decreased to 50 °C for the adsorption process with hydrogen gas for 60 min. After the adsorption process was completed, the system was retreated for 60 minutes with helium gas at 25 °C to remove any free hydrogen gas. Finally, the desorption of hydrogen gas started at 25 °C and increased at a ramp rate of 10 °C min^{-1} until 500 °C.

The initial dehydrogenation temperature of the CA samples was determined based on the obtained TPD curve. To demonstrate the significant role of Mg^{2+} as an enhancer in the synthesis of CA as hydrogen storage materials, the best concentration of CA samples with the highest desorption rate was chosen to compare with a pure CA sample. Besides, the best possible pore shape of the CA sample was determined based on BET analysis, and the morphology of CA sample was observed from FESEM image. Thus, the characteristics of the best CA sample as hydrogen storage materials were determined based on BET, TPD, and FESEM analysis.

3.5 Research Flow Chart



Objective 1: Synthesis of CA

Prepare pure CA and enhanced CA; different parameters in term of types and concentration of metal ions.	Comparison between pure CA and enhanced CA.

Objective 2: Characterisation of CA

FTIR, XRD, BET and FESEM analysis.	Study the CA samples in term of molecular, structural, morphology and porosity.

Objective 3: Ability of CA as a Hydrogen Storage Material

TPD analysis.	Determine the best CA sample based on desorption behaviour towards hydrogen gas.