

**METAL OXIDES SUPPORTED ON NITROGEN DOPED
CARBON BASED AS EFFICIENT ADSORBENTS FOR
CO₂ CAPTURE**

BY
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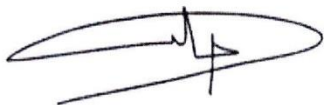
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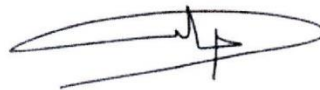
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I dedicate this work to Allah SWA and to my family and friends

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LIST OF ABBREVIATIONS

GZ-A : Activated Carbon

GZ-B : Nitrogen-doped carbon

GZ-C : Impregnated Cerium on nitrogen-doped carbon

GZ-D : Impregnated Manganese on nitrogen-doped carbon

GZ-E : Impregnated Calcium on nitrogen-doped carbon

APCs : Activated Porous Carbons

BET : Branauer, Emmett and Teller

BJH : Barrett, Joyner and Halenda

CCC : CO₂ Capture Capacity

MOFs : Metal Organic Frameworks

SEM : Scanning Electron Microscope

FTIR : Fourier Transform Infrared

XRD : X-ray diffraction

XPS : X-ray photoelectron Spectroscopy

SEM : Scanning Electron Microscope |

ABSTRACT

Full Name : Towolawi Saheed

Thesis Title : Metal Oxides Supported on Nitrogen-Doped Carbon Based as Efficient Adsorbents for CO₂ Capture

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The importance of agricultural waste or biomass as a precursor due to its low cost cannot be over emphasized. This property explains their usefulness in developing different sorbents for CO₂ capture. In this work, nitrogen-modified activated carbon was synthesized from a sustainable feedstock, groundnut shell, and melamine with impregnated metal oxides to investigate its viability as an alternative source of adsorbent in the capture of CO₂. Different characterization techniques majorly SEM, XRD, N₂-sorption, TEM, RAMAN and FTIR was used to determine the structural and physical properties of the synthesized materials. The as-synthesized adsorbent was evaluated for CO₂ capture, and the selectivity of the adsorbent in the stream of other gases, CH₄ was investigated. The result of this work proved to route an alternative innovative path for the synthesis of impregnated metal-oxide on nitrogen-doped carbon for adsorption processes.

Towolawi Saheed :الاسم الكامل

عنوان الرسالة: أكاسيد الفلزات المدعومة على كربون نيتروجين مخدر يعتمد على المميزات الفعالة لثاني أكسيد الكربون

التخصص الرئيسي: الكيمياء

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لا يمكن التشديد على أهمية النفايات الزراعية أو الكتلة الحيوية كسلائف بسبب تكلفتها المنخفضة. تشرح هذه الخاصية فائدتها في تطوير مواد ماصة مختلفة لالتقاط ثاني أكسيد الكربون. في هذا العمل ، تم تصنيع الكربون المنشط المعدل من النيتروجين من مادة خام مستدامة وقذيفة من الفول السوداني وميلامين بأكاسيد معدنية مشربة للتحقيق في قابليته للإنتاج كمصدر بديل للامتصاص في التقاط ثاني أكسيد الكربون. تم استخدام تقنيات التوصيف المختلفة بشكل رئيسي لتحديد الخصائص الهيكلية والفيزيائية للمواد FTIR و RAMAN و TEM و N2-sorption و XRD و SEM المركبة. تم تقييم المادة الماصة المركبة كمادة مخلقة لاحتجاز ثاني أكسيد الكربون ، وتم التحقيق في انتقائية المادة الماصة في مجرى الغازات الأخرى. أثبتت نتيجة هذا العمل توفير مسار مبتكر بديل لتخليق أكسيد المعادن المشرب . على الكربون المنشط بالنيتروجين لعمليات الامتزاز

CHAPTER 1

INTRODUCTION

Uncontrolled release of greenhouse gases (GHG) especially carbon dioxide CO₂ has threaten and still threaten the long ever-existing climate's morphological configuration and conformation in recent decades due to unavoidably excessive dependence on the burning of fossil fuel ignited by geometrical increase in the world's population [1]. Stern warnings and concerns have been raised should this continues unabatedly, that the world should envisage coming years of increased in climate's temperature which would inadvertently pose a negative effect to the entire universe.

Unfortunately, as at present, there are clear and undeniable indications that alternative sources of energy to fossil fuel are almost not available and those few in existence require not only extensive practicability but also the cost penalty must also be carefully considered. Therefore it becomes pertinent to mitigate the uncontrolled increase in the rate of CO₂ emission. Many concerned agencies and government parastatals have suggested different criteria and strategies in a bid to end the menace pose by CO₂ emission [2]

1.1 Environmental anxieties

The unending progressive escalation in the utility of CO₂ containing fuels coupled with, though steady, but consistent environmental activities in virtually all the nooks and crannies of the universe has inadvertently resulted in a sharp, unprecedented change in atmospheric morphology and conformation. This was linked to the birth of industrial revolution has greatly and geometrically challenged and opposed the climatic make up. The sudden change in the concentration of the greenhouse gases especially CO₂ spirked up unprecedentedly during this period with highly industrialized nation taking the lead. It has been noted that the United States and China are the frontiers in the emission list and this is expected because highly industrialized nation emit more compare to the less industrialized one. In the report released by Intergovernmental Panel on climate change, an intergovernmental body that keeps the world updated about the risk of climate change, its prevention and economic impacts maintains some line of arguments to establish that change in climate is unequivocal which emanated since the beginning of industrial revolution. The presence of these gases has caused global warming due to the shift in weather pattern [2].

As a result, the quality of the surrounding air has been affected due to the romance with CO₂-containing fuels. The cumulative effects of these gases especially CO₂ seeks to bring about a disorder in human health. The negative effect of these gases has more adverse impact in the lives of people whose daily bread depends solely on the urban area.

Bio ecosystem species are also affected adversely, as a result of the aforementioned; there is urgent need to curtail this daunting continuous challenge if we must have a stable pollution-free environment.

1.2 Technologies of CO₂ Capture

Various technological alternatives exist but only few were adapted in the industrial world. The CO₂ emission from a power plant which is a major source of CO₂ emission could be capture primarily using the technologies of either pre combustion, post combustion or oxy combustion and until recently Calcium looping making the fourth on the list. Each of which has its own pros and cons.

Pre combustion capture is a phenomenon whereby oxygen is used in the treatment of the primary fuels yielding hydrogen gas and CO₂ in a mixed ratio of 60:40 respectively. This will then be allowed to undergo the process of CO₂ separation leaving behind the pure hydrogen gas which can be later used for power generation. Plants with gasified integration are best captured using pre combustion method. Post combustion involves the use of amine-based solvents to capture CO₂. The stream of gas containing high amount of CO₂ is made to be in contact with amine-based solution which reversibly reacts with the CO₂ yielding water soluble salts. The process is well fitted for capturing CO₂ from stream of dilute and low pressure origin. This applicability defines its usage at stationary CO₂ source.

In oxyfuel combustion technology, the presence of oxygen of high percent purity facilitated combustion which is follow by recycle. The main feature of this technology is that it yields CO₂ and H₂O, the latter which can be easily removed through condensation and leaving behind pure stream of CO₂.

In calcium looping, a method similar to amine-based post combustion technology, there exist a reversible reaction between calcium oxide and CO₂, a reaction that produces calcium carbonate (CaCO₃) which occur in one vessel called the calcinator which is then passed unto

the second vessel called calciner vessel where regeneration takes place leaving a pure stream of CO₂ behind.

1.3 Methods of CO₂ Capture

Existing technological methods suitable for the capture of CO₂ are absorption, which may be (Physical or Chemical), membrane separation, cryogenic distillation and adsorption. The principle of absorption is primarily applicable to reactions involving CO₂ with solvent containing solutions of amine and its derivative. Despite its applicability, its uses is limited due to the difficulty involves in regenerating the solvent due to its cost enthalpy [3]. Cryogenic process is a method employed widely on a large scale to remove CO₂ from streams having high concentration of CO₂. This limits its application to streams containing dilute CO₂. One of its excellent merits is the production of liquid CO₂ and also does not involve the use of any chemical solvent. Its application has been limited due to the high cost penalty needed to prevent excessive water from ice plugging. Membrane technology, on the other hand, is a selective method of which employs membranes to dissect compounds of certain materials from a gas stream. Membranes are selectively permeable materials with potential use of varying mechanism to separate substances. It has different advantages some of which are but not limited to low energy requirement when compared to absorption and cryogenic methods but its application is limited by the ability and capability of adsorbent available for CO₂ capture, low selectivity leading to low efficacy of percentage removal as well as possibility of reuse of the adsorbents. [4]

1.4 Adsorption

Adsorption could be said to be a phenomenon whereby gases or liquid are bonded or adapted to a surface of solid matrix. Adsorption possesses the inherent capacity to positively alter the energy as well as the cost penalty involved in the capture of CO₂. Conversely however, easy regeneration and durability of the developed adsorbent that affords enhanced adsorption capacities defines the potency of the this method.[1-4]

Chemical adsorption or chemisorption and Physical adsorption or Physisorption are the two major forms of adsorption mechanism that that exist.

Chemisorption, a category of adsorption, employs reaction at a surface that has been exposed using metal oxide and metal salts. Despite its viability, arduous regeneration strength and necessity for more studies challenges its wide applicability. Physisorption on the other hand, is a method that works on the principle of perturbation of the electronic make up of the atom. The chemistry of adsorption uses the intermolecular forces of attraction between gases to be separated and the surface of the active material which could be an activated carbon or molecular sieves. This method is very advantageous due to its extremely low cost because most of the precursor for activated carbon is sourced from agricultural waste produce or biomass [5].

1.5 Criteria for choosing CO₂ sorbent material

Selection of appropriate CO₂ sorbent material is most times a complicated and tedious decision as important parameters such as economical and operational implications are needed to be duly considered to design an effective CO₂ sorbent material.

Different parameters are necessary to be considered when designing a sorbent for CO₂ capture, some of which are cost of sorbent, Selectivity for CO₂, Adsorption capacity for CO₂, easy regeneration of Sorbent and Adsorption/ desorption kinetics.

Cost of sorbent is relatively the most important of all the enumerated parameters as all others revolve around it. This is because the wide applicability of any sorbent will be geometrically affected if its cost penalty is not economically friendly.

CO₂ selectivity is another important factor that needs to be considered. Selectivity is a measure of how effective a sorbent is in adsorbing CO₂ relative to other gas components. This is very essential as it has an effect on the purity of CO₂ adsorbed.

Adsorption/ desorption kinetics is also of utmost importance as it relates the kinetics of adsorption/desorption to the effectiveness of CO₂ capture by studying the effect of functional group present.[19]

1.6 Objectives

The main research objective is to design, synthesize, characterize and evaluate the efficacy of metal oxides over nitrogen doped carbon based support for CO₂ capture in the presence of CH₄ and N₂. The future goals and/or benefits of this research activity are as follows,

1. Capture CO₂ using nitrogen-doped carbon solid support impregnated with a novel metal oxide.
2. Characterization using different spectroscopic technique.
3. Varying the various amount of metal oxide to be impregnated on the nitrogen-doped carbon

4. Investigating the effect of varying different concentration of the activated carbon and melamine which serves as the nitrogen source.

1.7 Significant of the study

[. This research will avail low cost precursor with high surface area and metal dispersion, high CO₂ capture, and the potential regeneration for recyclability, from commercially cheap available starting materials.

Series of modified impregnated metal oxides over nitrogen-doped carbon supports will be synthesized by carbonization and activation followed by annealing the mixture at optimum temperature with heating rate of 5 °C min⁻¹ and hold for 2 hours under N₂ protection of 150mL min⁻¹ in a TL1200 tubular furnace.

Extensive characterization techniques will be adopted to gain insight into the physico-chemical properties of the activated carbon, nitrogen-modified carbon and modified metal oxides impregnated on nitrogen-doped carbon. Surface area and porosity analyzer will be used for textural properties information of the activated carbon, nitrogen-doped carbon, and impregnated metal oxides over nitrogen-doped carbon.

CHAPTER 2

LITERATURE REVIEW

2.1 General Overview

Considering the existing route used to capture carbon dioxide, Post combustion capture is recognized as the most viable system due to its flexibility and maturity [1,6]

There exist numerous processes used in the separation of carbon dioxide using the post combustion method involving solvents of amine origin. The encountered challenges faced when employing this method include but not limited to loss of solvent, cost contingencies and more importantly, relatively lower amount of carbon dioxide pressure in the flue gas.[7]

Adsorption using materials of solid nature could be employed to surmount the hurdles created by the former method as a result of its inherently low energy penalty, small capital intensive and the reasonable cost of operation [8,9,10]

Different parameters dictate the efficacy or the viability of various adsorbents used in capturing carbon dioxide (CO₂) which are majorly the mesoporosity and microporosity of adsorbent which is a function of the pore attributes. The type of pore present in an adsorbent has been classified according to the size of the cavity present [11].

There have been propositions made for CO₂ adsorption using varying adsorbents each with its own defined attributes and merit. They include Activated carbon [12, 13], Zeolites [14], metal organic frameworks [15]. Of all these, Activated carbon has been regarded as a viable

adsorbent of solid origin that can be used in the capture of CO₂ due to the fact that it is cheaply available, flexibility for regeneration, practically employable at ambient temperature and relatively low energy enthalpy.[16]

In spite of the fact that they possess these interesting features, their wide applicability is put to questions due to some of their demerit which involve poor selectivity as well as uneven dispersion in media of different properties.

In the recent work of Siriwardane et al. [17,18,19] using molecular sieve and activated carbon, the adsorption capacity of CO₂ was investigated at elevated pressure, it was revealed that the activated carbon showed higher CO₂ adsorption ability than the corresponding molecular sieves[20,21,23,24,25].

2.2 Zeolites

Zeolites are regarded as non-amorphous alumino-silicate sorbent faciled in a non-random exposed configuration. The change in their morphology is predicated on varying parameters ranging from the ratio of silicon to Aluminium(Si/Al), respective orientation size and shape coupled with the nature of cage present.[26,27]

Type A and X zeolites have received unmatched attention so far as viable adsorbents for carbon capture. Their special features which afford their high CO₂ capability at ambient pressure account for their use as a potential sorbent for CO₂ capture. In general,13X, a special type of zeolite has been identified as a consistent material for CO₂ capture due to its high CO₂ capture update coupled with an excellent high selectivity experimented to be 2mmol/kg under a pressure of 0.1 bar at ambient temperature.

One of the major disadvantage usually encountered in using zeolite as an adsorbent for CO₂ capture is its hydrophilicity nature. In spite of the fact that they possess superb adsorption features, the inhibitive effect of the electric field is usually the challenge in the presence of water thus affecting the succinct interaction between the cation and the CO₂ to be captured thereby leading to significantly low output.

In the work of Brandani and Ruthven [28, 29], as well as Lee et al[30] and Li et al[31], it was concluded that significantly small amount of water is enough to geometrically affect the efficacy of zeolites. Also, another important factor that dictates how effective zeolites are for CO₂ capture is how cation are facilely oriented and distributed over the aluminosilicate framework which may either enhance or inhibit its capability, the more the charge density, the higher the uptake.

Lastly, one other necessary factor to be considered when using zeolite as a sorbent for CO₂ capture when there is a distortion in the zeolite structure due to cation blockage of the framework.

The amalgamation of the distortion of the morphological framework as discussed recently Lozinska et al, and the blockage effect of the cation induced a substantial reduction in the potency of zeolites' applicability. The result is similar to the conclusion of Palomino et al [32].

2.3 Metal Organic Frameworks (MOFs)

MOFs are non-uniform hybrid combination of both organic and inorganic network comprising bonds of metal to ligand. The ability to tune their properties (both structural and functional) afford their parameter like surface potential, dimension of the pore and channels configuration to be varied which in turn improve their inherent properties to favor their applicability in CO₂ capture.

In comparison to zeolites, MOFs exhibits higher CO₂ adsorption only at an elevated pressure. Only MOF-74 and its group have been found to have displayed its viability at ambient pressure for CO₂ capture. Various viable metals used in MOFs include but not limited to Magnesium, Nickel, Cobalt and Zinc, each of which act as the central atom in the framework of metal-ligand network.

Magnesium when bonded to MOF-74 showed the highest carbon capture uptake followed by nickel, cobalt and then zinc. Enhanced ionic affinity between magnesium and MOF-74 has been adduced to this higher uptake. This will inadvertently make magnesium to be hydrophilic in comparison with other metals.

When the effect of hydrophilicity was investigated in a research undertaken by Le Van et al [33], for all zeolites obtained commercially compared with Ni-MOF-74, it was shown that the latter showed lesser effect to hydrophilicity due to the lesser or little electron affinity between it and Mg-MOF-74. Liu et al recorded the same observation. [34]

2.4 Activated Porous Carbon (APC)

This is a class of solid sorbent used in the adsorption of CO₂. The synthesis of activated porous carbon stems from decomposing thermally, materials of carbon source especially biomass from agricultural waste material. An extensive journey on the applicability of APC has been undertaken by various scientists for some years back. Of all the existing solid sorbents, activated porous carbon has been regarded as one of the most effective sorbents owing to its inherent distinct features ranging from its ubiquitous nature, chemical robustness and an unmatched surface area.

Recently in the literature, a BET surface area of 862 and 1215m²/g has been shown for almond and olive stones that have been activated with carbon capture capacities (CCC) of 2.7 and 3.1mmol/g respectively [35]. Current enhancements in APC method pave way for scientists to achieving higher surface area through different novelty.

A surface area of 4200m²/g was achieved through various doping methods at high pressure in the recent research of Jalilov et al [36] achieving a CO₂ adsorption capacity of approximately 2.6mmol/g. Utilization of APC of high surface area marred with nitrogen groups is another method scientist explore to enhance CO₂ adsorption capacity.

The effect of various doping methods was investigated in the research of Zhang et al using APC of relatively high surface area to enhance CO₂ viability which varies between (2.93-3.95mmol/g). When APC was compared to zeolites, in a research endeavor by Siriwandane et al, APC showed lower CO₂ adsorption capacity at ambient pressure, the same observation was concluded on by Shan et al [37]

APC of aromatic polyaniline origin sequel with nitrogen-containing group has also demonstrated high level of CO₂ adsorption efficiency of 4.3mmol/g.

Recently, researchers have been seeking for a compatible modification of Porous Activated carbon (PACs) due to their disadvantages of low uptake, poor selectivity and relatively physisorption-dependent mechanism which may inhibit its application to flue gas with low partial pressure [38,39]. To this end, two methods have been employed to enhance CO₂ adsorption efficiency of PACs.

The first method involve the expansion of surface area of PACs through either chemical activation or pyrolysis yielding PACs of well expanded pore structure of both mesoporous and microporous configuration. The second method makes use the building of basic sites with the aid of basic functionality into the PACs network using the activation process since the CO₂ to be captured is weakly acidic [40,41,42,43,44]. Serilla et al. using N-enriched PACs recorded CO₂ adsorption uptake efficiency of 3.9mmol/g at 25°C [40]. Ma et al. recorded an enhanced CO₂ uptake capacity of 4.57mmol/g at 25°C and at 1bar with chemical activator, sodium arginate using N-doped carbon monolith [42]. These results revealed that with appropriate modification of PACs surface chemistry, an interesting highly enhanced CO₂ uptake may results.

Conversely however, there is a drawback of poor selectivity and low adsorption uptake especially at an atmospheric pressure lesser than 1 bar associated with PACs fashioned in this way.

To surmount this drawback hurdles, we seek to employ the use of nitrogen-containing precursor, melamine, follow with post modification with series of metal oxides impregnated at varying weight percent probing the surface chemistry to enhance stronger

interaction. Many researchers have investigated and evaluated the viability of metal based solid sorbents for the capture of CO₂ [45,46,47,48,49,50,51], but the dual impact of the use of nitrogen functionality and incorporation of metal oxides has been hardly reported so far.

CHAPTER 3

MATERIALS AND METHODS

3.1 Chemicals and materials

Groundnut shell (Original source of carbon precursor), Melamine (source of nitrogen), zinc chloride, Magnesium oxide, Manganese nitrate, calcium chloride, Cerium nitrate and distilled water. All the chemicals were sourced from Sigma-Aldrich. Highly purified distilled water was made available with the aid of Labstrong FiSTREEM II 2S Glass Still distiller.

3.2 Carbonization of Groundnut Shell

Weighing an equivalent amount of the precursor, groundnut shell alongside with the chemical activator, a reagent that enhances pyrolytic decomposition of the carbon based material, zinc chloride initiates the early stage of the carbonization process. A 1:1 ratio of the precursor to the activator was weighed into a 250mL beaker after which a known amount of distilled water was added to it up to the level just above the mixture and was stirred for about four hours at 600 rpm operated at room temperature for the first three hours and at 400 rpm operated at 60°C to ensure uniformity and avoid agglomeration between the mixture using a stirrer which was later transferred into an oven for about 12 hours for calcination. The resulting mixture was later transferred into the furnace with the aid of a crucible. The operational condition of the furnace under the flow of Nitrogen, N₂ was set to be

150cm³/min at a ramping rate of 10°C/min up to 900°C and was held under this condition for two hours. Upon cooling the furnace, the resulting material is a carbonized mixture designated as GZ-A.

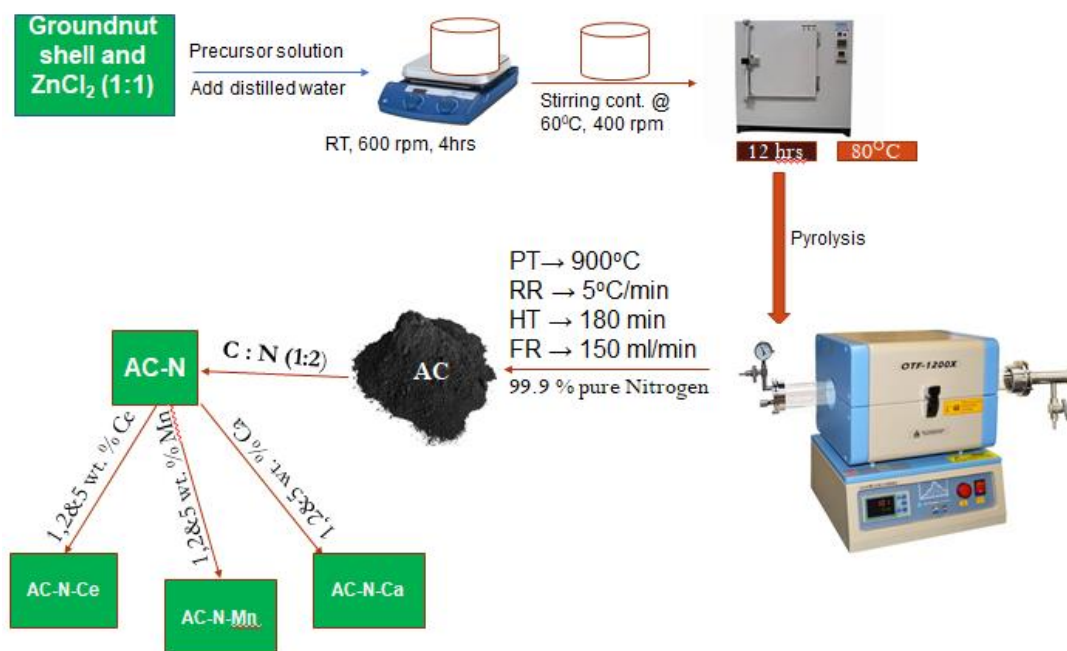


Figure 1: Graphical Chart

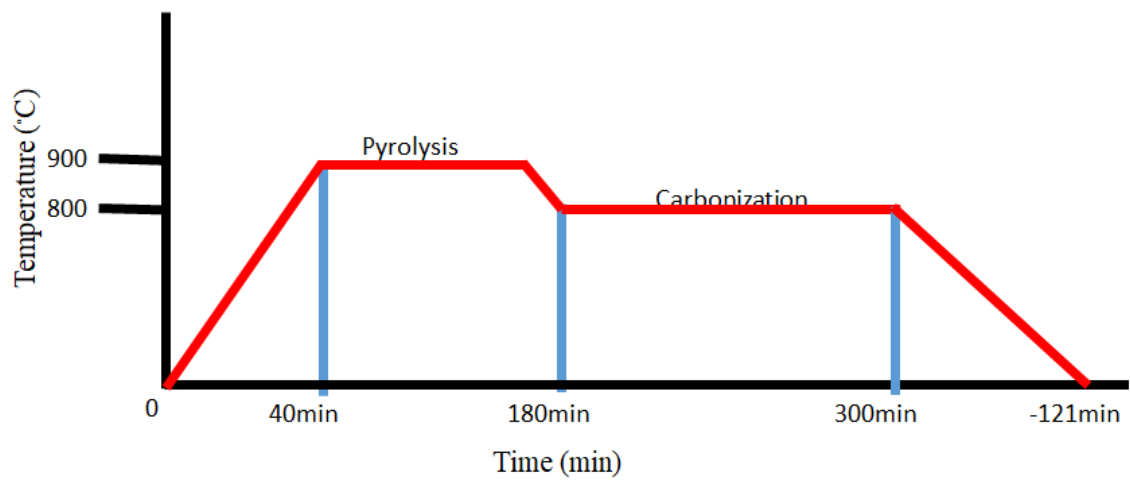


Figure 2: Pyrolysis and Carbonization Chart

3.3 Nitrogen-doped Activated Carbon

After the activated carbon has been synthesized, varying ratios of 1:1, 1:2 and 1:3 activated carbon to melamine (which is the source of nitrogen) was duly investigated to establish and ascertain viable optimum working conditions. To this end, accurately weighed and uniformly mixed with the aid of mortar and pestle were carried out for each sample ratio. The resulting mixture was then transferred into a crucible and put into the furnace operated at a condition of temperature of 600°C at a ramping rate of 10°C/min held for one hour under Nitrogen, N₂ gas at 150cm³ /min. This becomes pertinent in order to ensure an even distribution or spread out of the nitrogen on the surface of the carbon. The resulting mixture is designated as GZ-B.

3.4 Incorporation of Selected Metals

In an effort to further probe into the possibility of CO₂ capture enhancement by the nitrogen-doped activated carbon, selected metals were impregnated on the GZ-B.

The effect of varying weight percent of the metals were investigated, specifically 1%, 2% and 5% percent weight to ensure if there is any enhanced and supported metal- surface interaction. A known amount of GZ-B was thoroughly mixed with an accurately weighed percent of the respective metals in a mortar and then transferred into the furnace at an operating temperature of 600°C at 10°C/min ramping rate held for one hour. Upon cooling of the furnace, the sample was removed and consequently labeled as GZ-C, GZ-D and GZ-E.

3.5 Adsorbents characterization

The sorbents materials, GZ-A, GZ-B, GZ-C, GZ-D and GZ-E were allowed to undergo extensive and highly exhaustive characterization so as to establish their physico-chemical and structurally related properties. This is very necessary because the changes observed from sorbent synthesis should be able to provide an insight and detailed mechanism of what is happening at different sorbent stage, especially that related to the changes observed when nitrogen was introduced and also the selected metals in terms of the surface area whether enhancement or inhibition.

Starting from phase characterization, Rigaku Ultima IV X-ray diffractometer was used and operated using energy of 40kV and a current of 40mA with a limit of 5°-60° 2 θ at a

velocity of 5°/min. Macromeritrics ASAP 2020 was employed to determine the physical textural attributes of the sorbents under study to probe the pore size and volume using the Barrett, Joyner and Halenda(BJH) approximation method while Branauer, Emmett and Teller(BET) reveals the nature of the surface area. The sorbents were carbonized using a furnace operated at 900°C at a ramping rate of 5°C/min held under this conditions for two hours under nitrogen gas at a flow rate of 150cm³/min. The frequency of synthesized varying sorbents was determined using Thermo scientific Nicolet 6700 FTIR Spec(400-4000cm⁻¹). The samples were pretreated by mixing with KBr in a stoichiometric ratio of 1:100 formula in order to form a pellet of the synthesized materials with the aid of AtlasTM press. Sample holder was used to hold the disc of the pellet formed which was later focused on the source of RI for the reading to be taken. The RAMAN analysis was also employed to ascertain if there was any possibility of the presence of graphitic or amorphous carbon. The structure and morphological orientation of the sorbents were determined with the aid of Field Emission Scanning Electron Microscope using a secondary electron (BSE) with 20kV accelerated voltage.

X-ray photoelectron spectroscopy (XPS) of PHI 5000 Versa Probe II, ULVAC-PPII Inc.

Finally, In a bid to determine the CO₂ capture capacity, the orientation of the microsize pores at 298k was determined using CO₂ adsorption isotherms. Contaminants and other unwanted materials were eliminated by degassing for hours under high vacuum.

CHAPTER 4

RESULTS

4.1 XRD

The very versatile non-destructive technique, X-ray diffraction was used to probe the properties of the synthesized sorbents structure alongside with the spatial orientation. The XRD features all the synthesized sorbents starting from GZ-A to GZ-E is presented chronologically in Fig 5. GZ-A, according to its observed broad peak, an amorphous nature ensued separately at 23° and 43° , which is a strong indication that the activated carbon is without any doubt amorphous in nature. Upon in-cooperation of metals to the nitrogen-doped carbon, the XRD patterns for GZ-C, GZ-D, and GZ-E do not show any succinct special features and attributes. This may be an indication that a concomitant and well dispersed relationship exist between the metals and the impregnated surface.

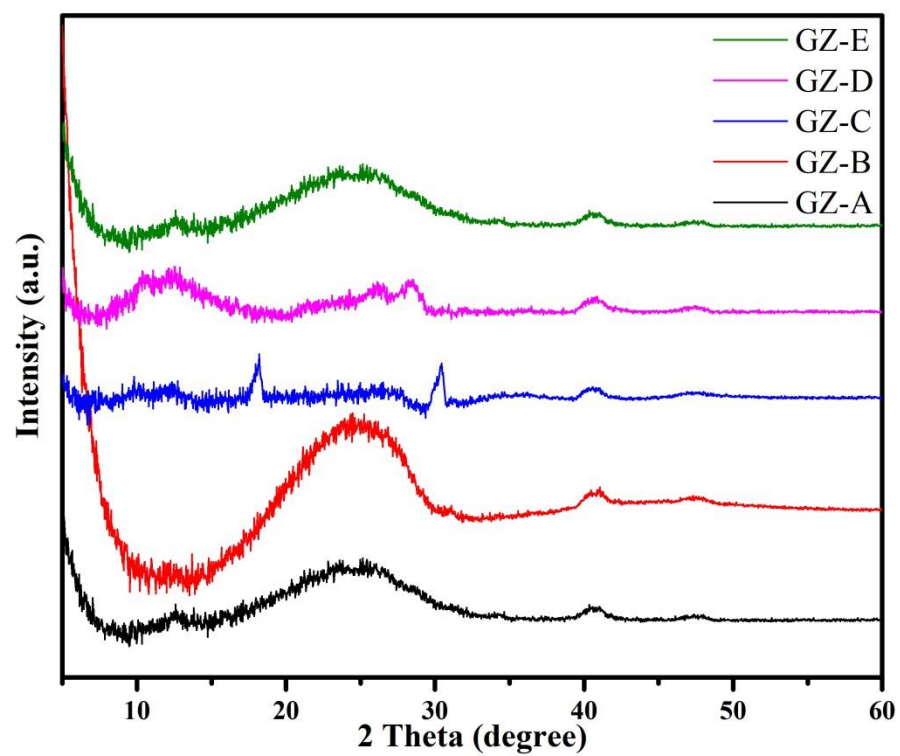


Figure 3: XRD Image of (a) GZ-A (b) GZ-B (c) GZ-C (d) GZ-D and (e) GZ-E

4.2 BET Surface area

The nitrogen adsorption and desorption isotherms were investigated in order for the surface morphological chemistry to be revealed. The parent material, GZ-A, alongside with all its derivatives (GZ-B, GZ-C GZ-D and GZ-E) were properly investigated. From the plot below, it can be inferred that the observed Isotherm for the parent material is Type 1, if the IUPAC system of classification is to be adopted [52,53]. The BET Isotherm of Type 1 is characteristics of microporous activated carbon with little or no mesoporosity[54,55]. This type of Isotherms is common to materials of pore size dimension that spans a definite range of encompassing majorly micropores with minor mesopores ($< \sim 2.5\text{nm}$). On the contrary, The observed Isotherms elucidated for its derivatives subtly revealed Type IV. The Type IV Isotherms, according to IUPAC, are exclusive characteristic of adsorbents that are mesoporous due to presence of hysteresis Loop. Type IV BET Isotherms feature an adsorption containing both microporous and mesoporous nature thus accommodating monolayer-multilayer system of adsorption with the presence of pore condensation. Comparing the parent material, GZ-A to the nitrogen-doped activated carbon, GZ-B, a slight reduction was observed in the surface area of the latter which may be partly attributed to the presence of nitrogen which might have occupy some vacant site on the on the surface of the parent material thereby reducing the total number of active surfaces available for adsorption. Similar trend was also observed when metals were loaded on to the surface of GZ-B except for manganese which possesses higher value than GZ-B. To explain this discrepancy, it is pertinent to further investigate why the value is higher

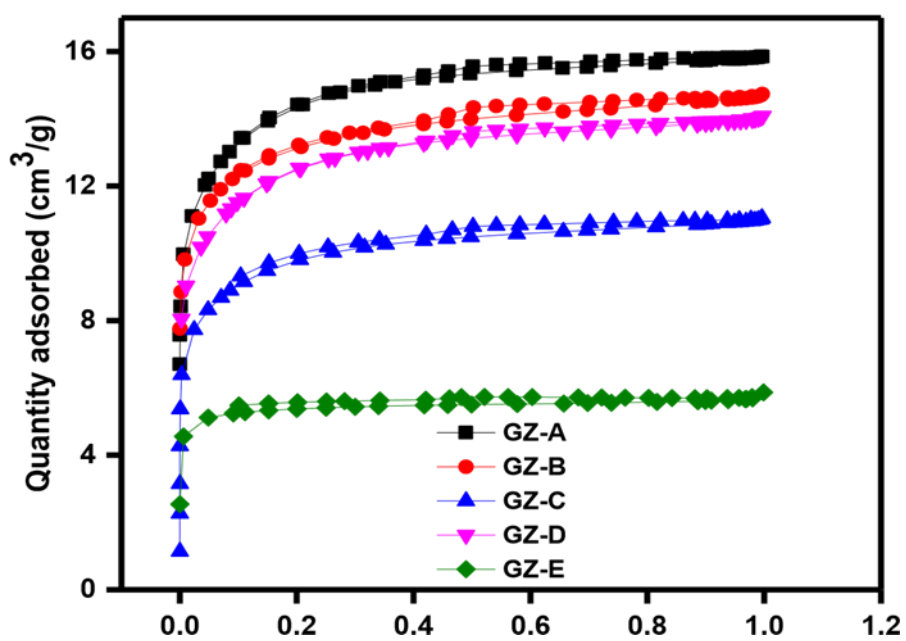


Figure 4: Nitrogen adsorption-desorption isotherm for (a) GZ-A (b) GZ-B (c) GZ-C (d) GZ-D, and (e) GZ-E

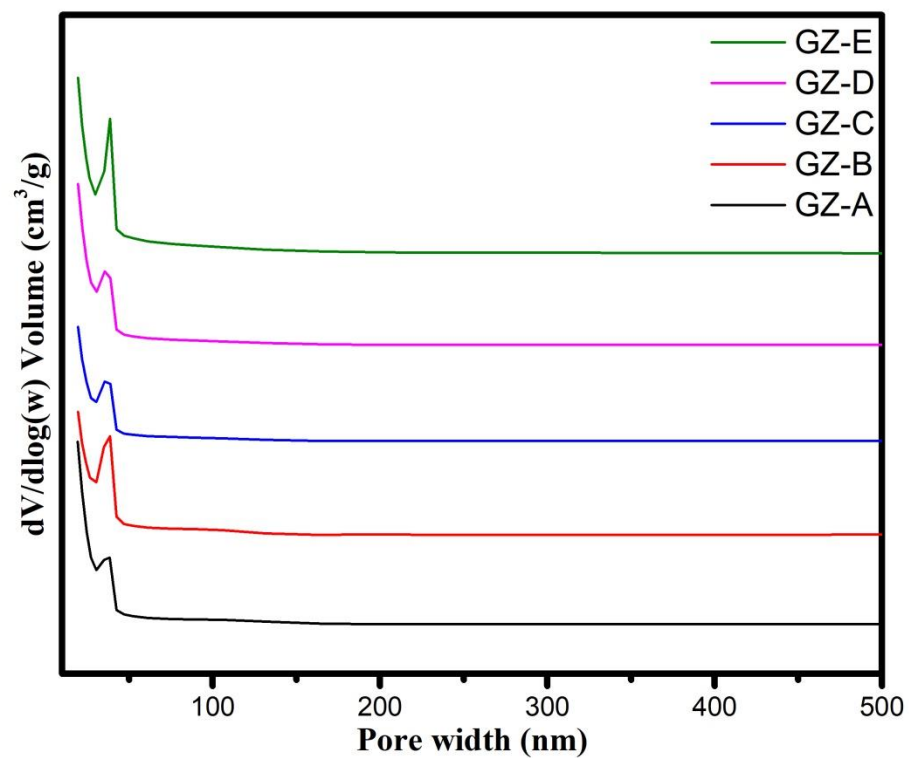


Figure 5: Pore distribution of (a) GZ-A (b) GZ-B (c) GZ-C (d) GZ-D, and (e) GZ-E

Table 1: Textural properties of Adsorbents



Support	BET Surface Area (m²/g)	Microporous Surface area (m²/g)	Mesoporous surface area (m²/g)	Microporous pore volume (cm³/g)	Total pore volume (cm³/g)	Average pore size (nm)
GZ-A	1184	538	646	0.22	0.54	2.5
GZ-B	1088	624	464	0.26	0.50	2.6
GZ-C	807	373	434	0.15	0.38	2.8
GZ-D	1026	431	595	0.18	0.48	2.7
GZ-E	1125	460	665	0.19	0.54	2.9

4.3FTIR

The observed FTIR spectra revealed for the parent activated carbon material, GZ-A, revealed the presence of some specific bands at $(3500-3300) \text{ cm}^{-1}$ which is a strong indication of the presence of O-H stretching bond. In addition, there is another visible peak present at $(2350-2000) \text{ cm}^{-1}$ which could be related to the presence of carbon dioxide. On the introduction of melamine, a somewhat less broad peak was observed at a wavelength of $(3400-3200) \text{ cm}^{-1}$ which may strongly be indicative of presence of N-H bonds emanating from the introduced melamine. A reduction in intensity of the N-H bond was observed on introduction of different metals. This may be link to the fact that some of the metals might have been dispersed on the melamine. Also a peak around 1670cm^{-1} which could be assigned to C-N of heterocycles and lastly a peak around 690cm^{-1} is indicative of amorphous carbon.

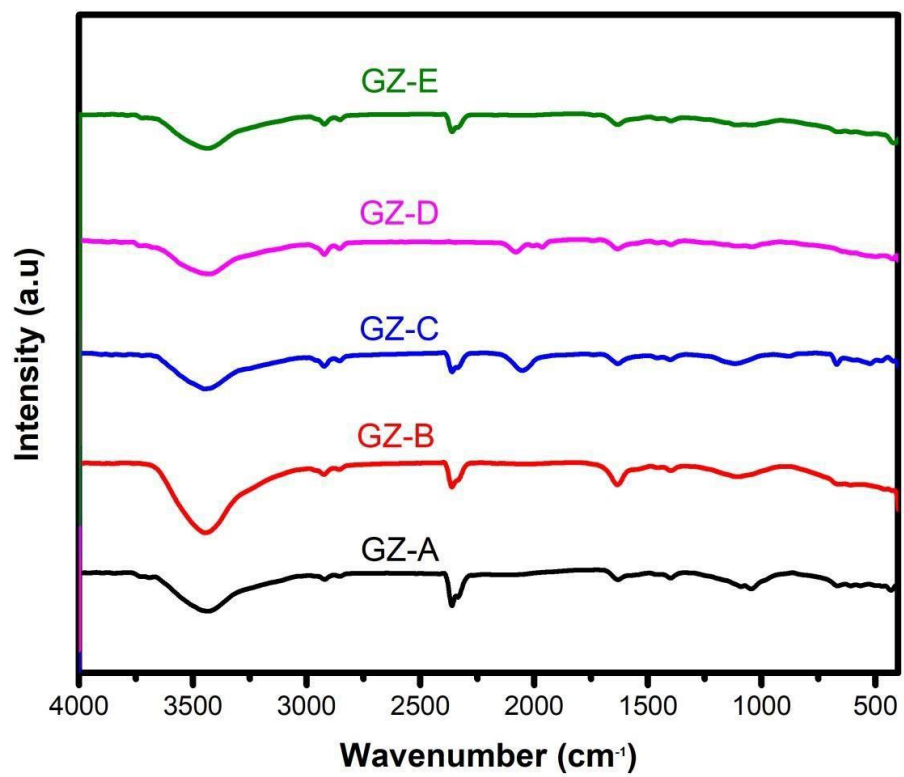


Figure 6: FTIR of (a) GZ-A (b) GZ-B (c) GZ-C (d) GZ-D, and (e) GZ-E

4.4 RAMAN

In order to verify the extent of structural orderliness and existence of defects in materials having graphitic potential, Raman spectroscopy was used to probe the microstructure morphology of the synthesized adsorbents. The result revealed the existence of a dual bands observed respectively at 1350cm^{-1} and 1590cm^{-1} , the former being partly due to carbon while the latter could be traced to the existence of nitrogen-modified activated carbon. The encountered dual bands could be linked to be typical of the D and G bands of amorphous graphitic carbon as can be evidenced in Figure 8. The absence of an intrinsic but less intense peak usually associated with a highly enriched graphitic carbon around 2300cm^{-1} to 3000cm^{-1} is a key indicator that all the synthesized materials possess a relatively lower graphitic to amorphous ratio. It is worth mentioning that the intensity of both the D and G bands increases as metals are incorporated with no additional or special peak being observed which may be due to higher degree of disorderliness in amorphosity.

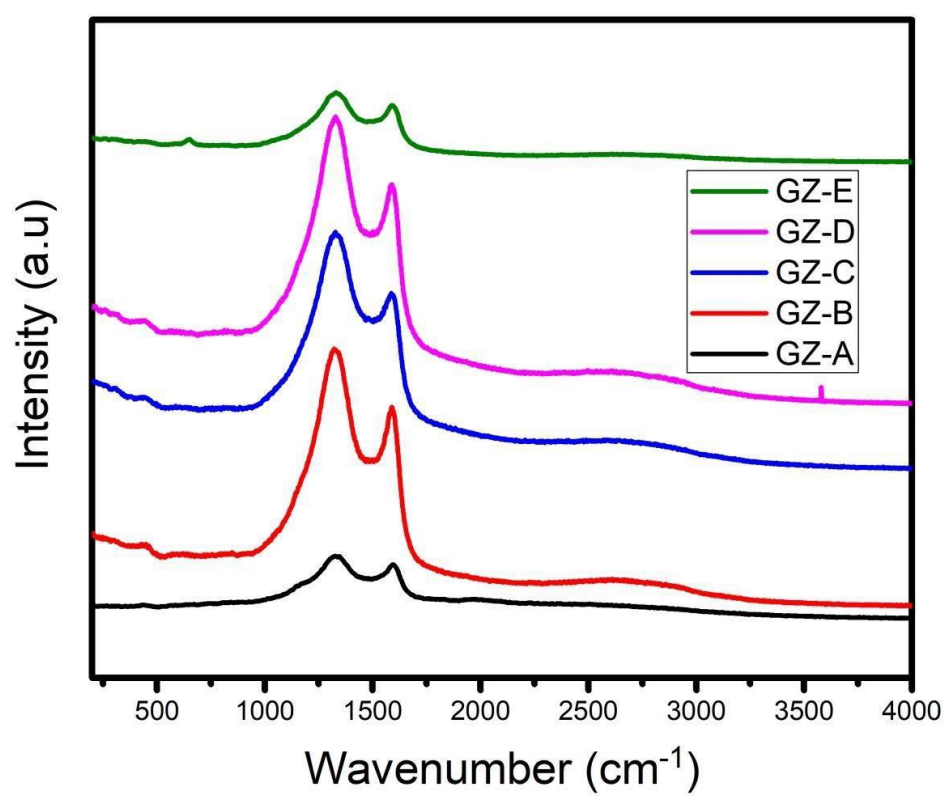


Figure 7: RAMAN spectrum of (a) GZ-A (b) GZ-B (c) GZ-C (d) GZ-D (e) GZ-E

4.5SEM

The results obtained for the scanning electron microscope revealed that GZ-A appeared to be made of flake-like surfaces with intertwined microporous pores while the rest, GZ-B, GZ-C, GZ-D and GZ-E was observed to have a connected network of mesoporous surface in an haphazard array. The dispersion of metals on the surface resulting from the SEM/EDS also revealed the mapping of the elements present. Conversely however, a poor metal dispersion was noticed for GZ-D as the metal was introduced. A concentration of metal was found not uniformly dispersed throughout the surface of the adsorbent and this may inadvertently affect the potency of the adsorbent, the extent to which can only be determined by testing the said adsorbent's potential for carbon capture.

Electron Image 1

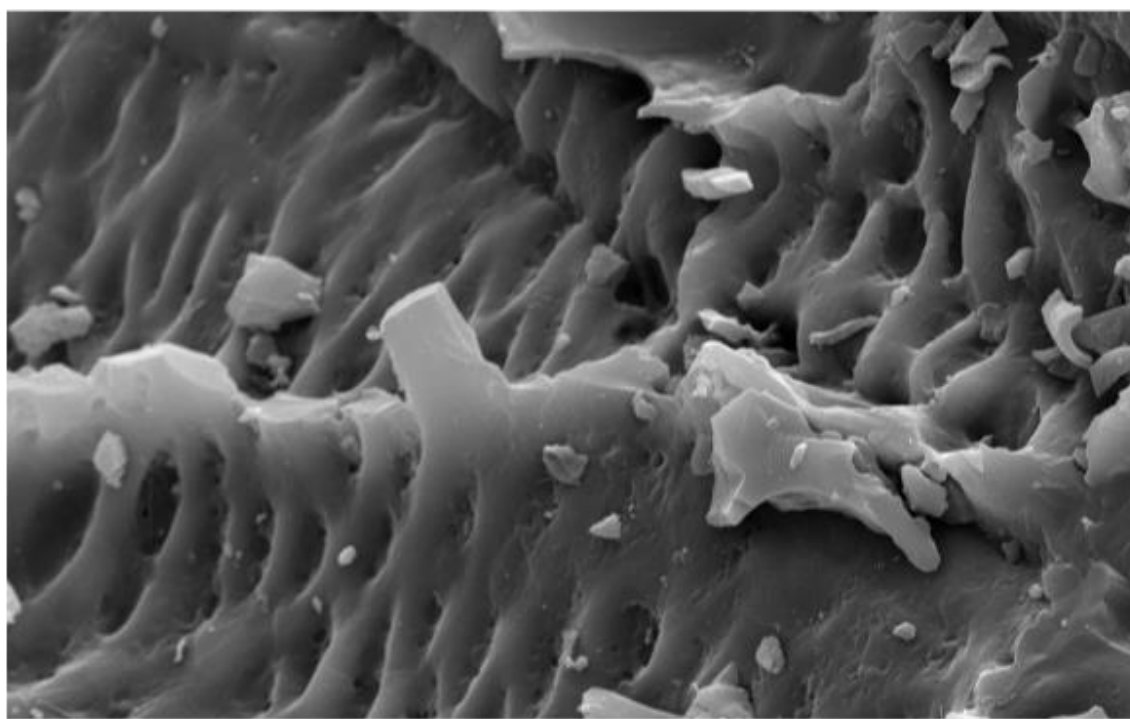


Figure 8: SEM image of GZ-A

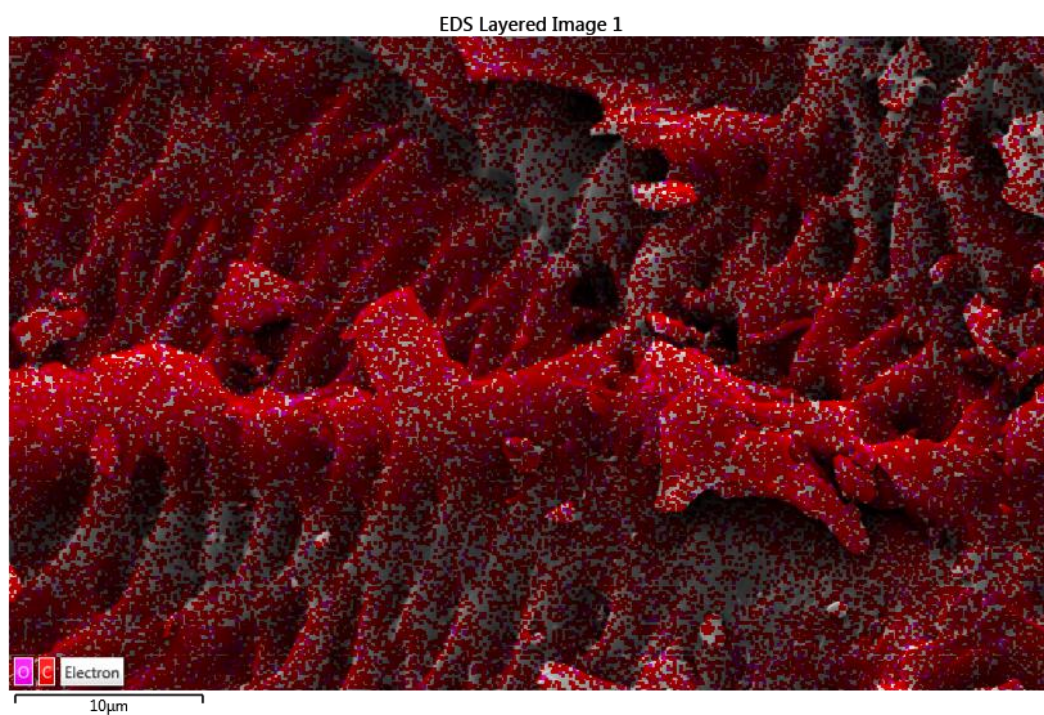


Figure 9: SEM/EDS Elemental mapping of GZ-A

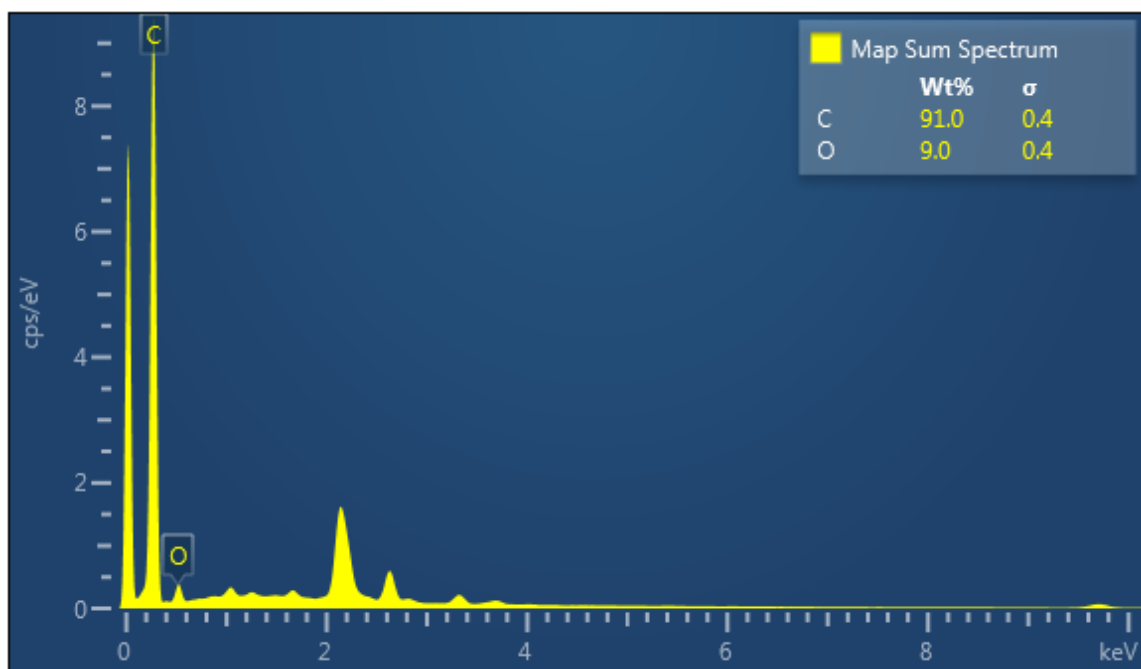


Figure 10: EDS spectra of GZ-A

Electron Image 1

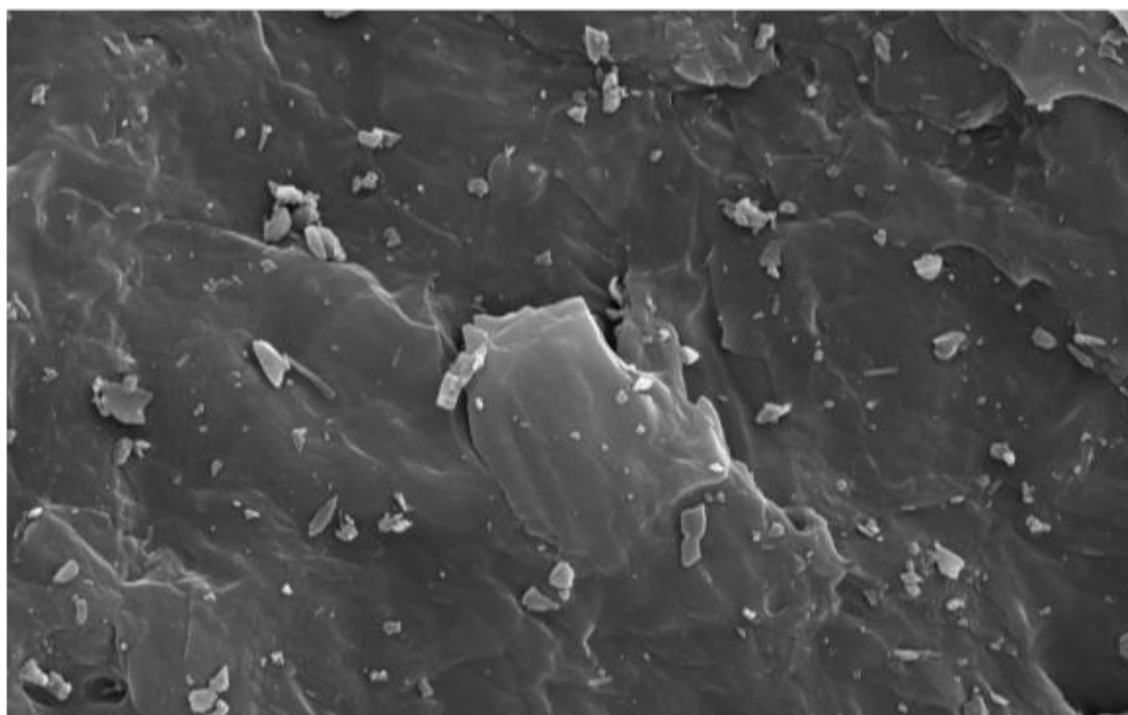


Figure 11: SEM image of GZ-B

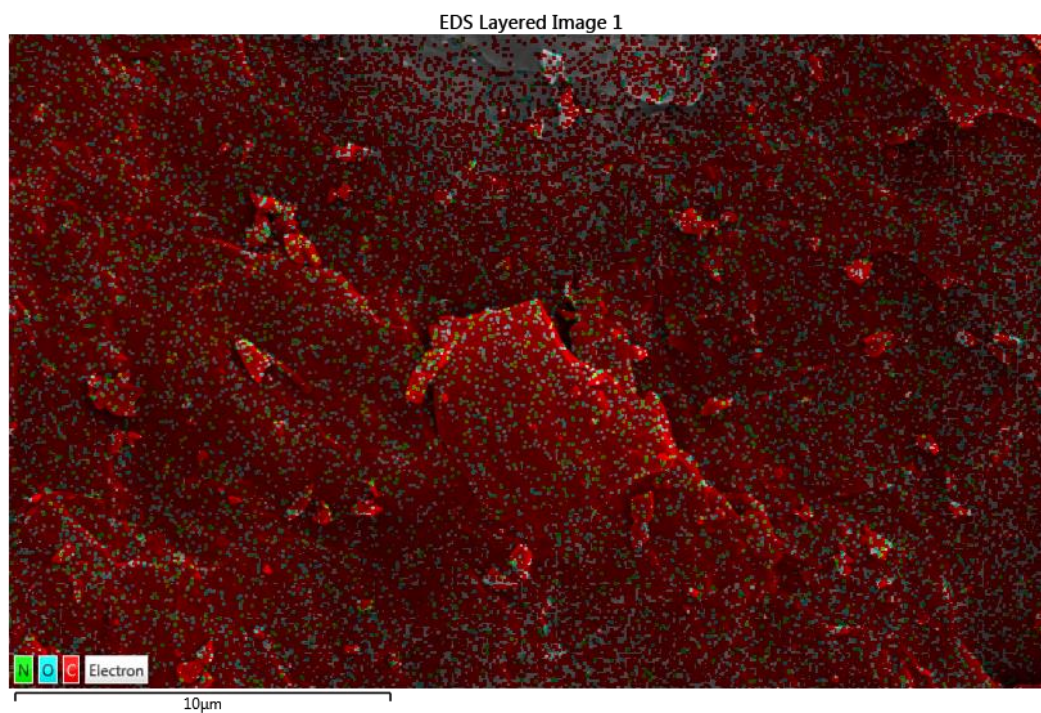


Figure 12: SEM/EDS Elemental mapping of GZ-B

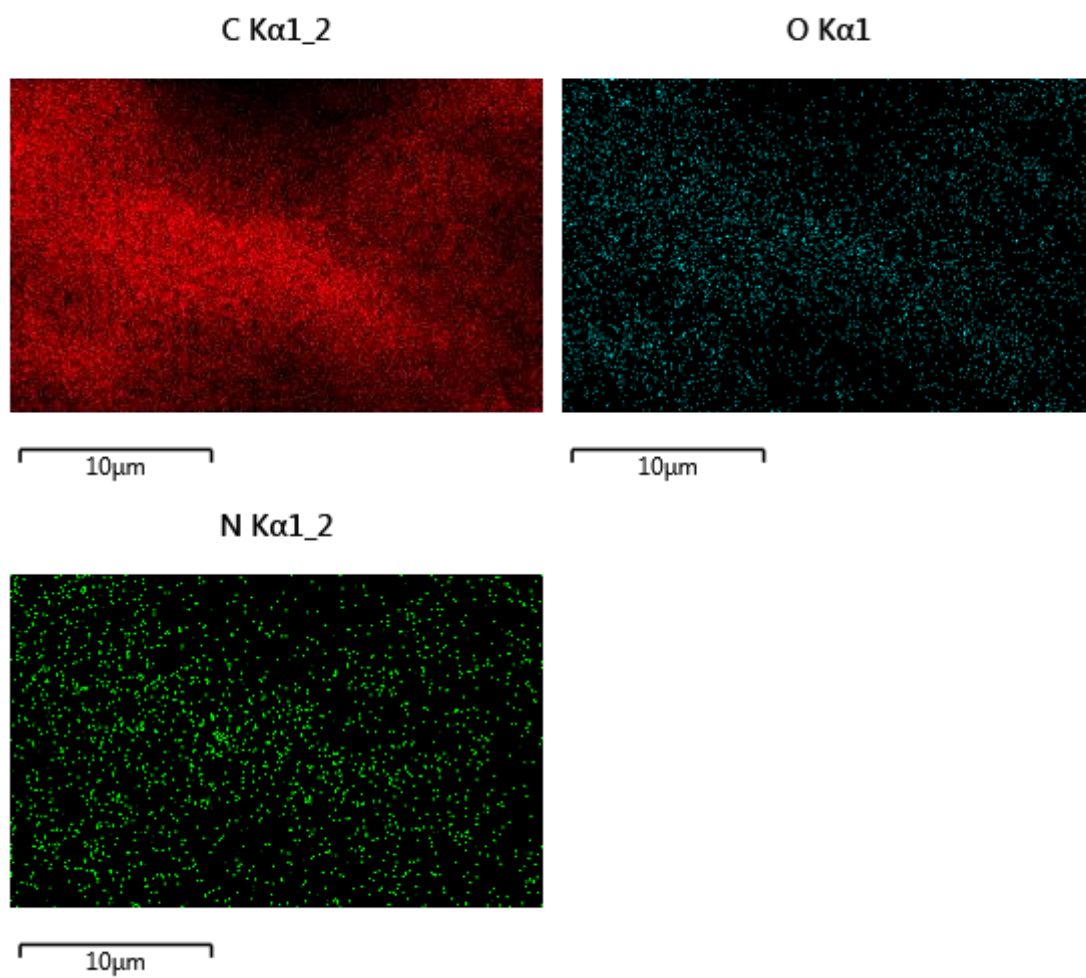


Figure 13: EDS mapping of C, O, and N of GZ-B

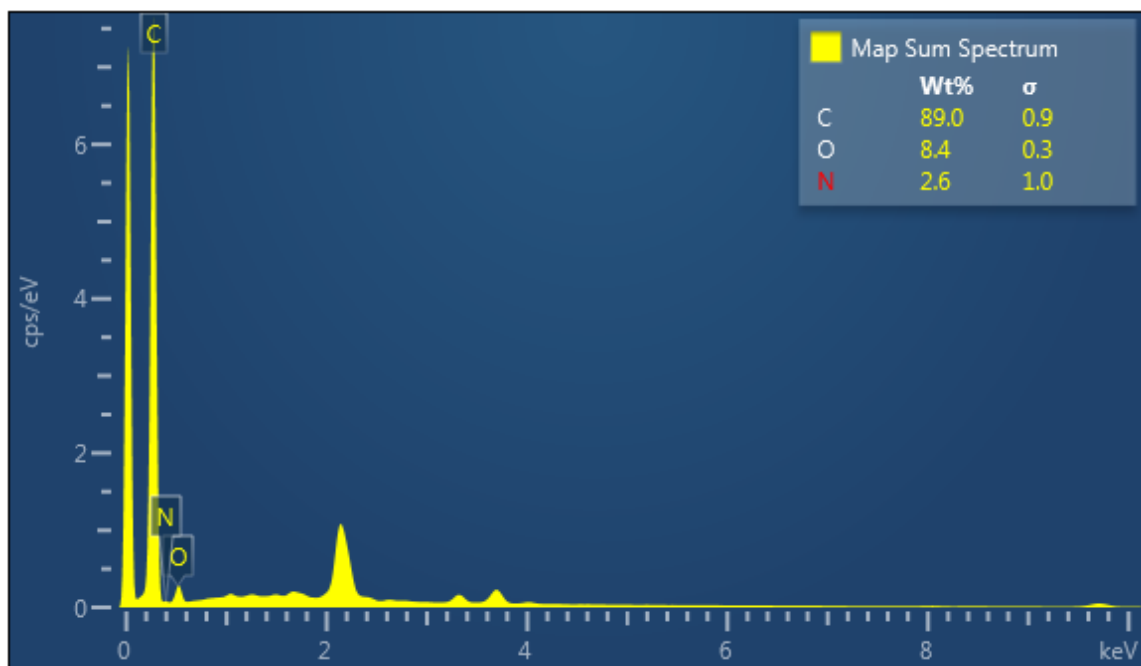
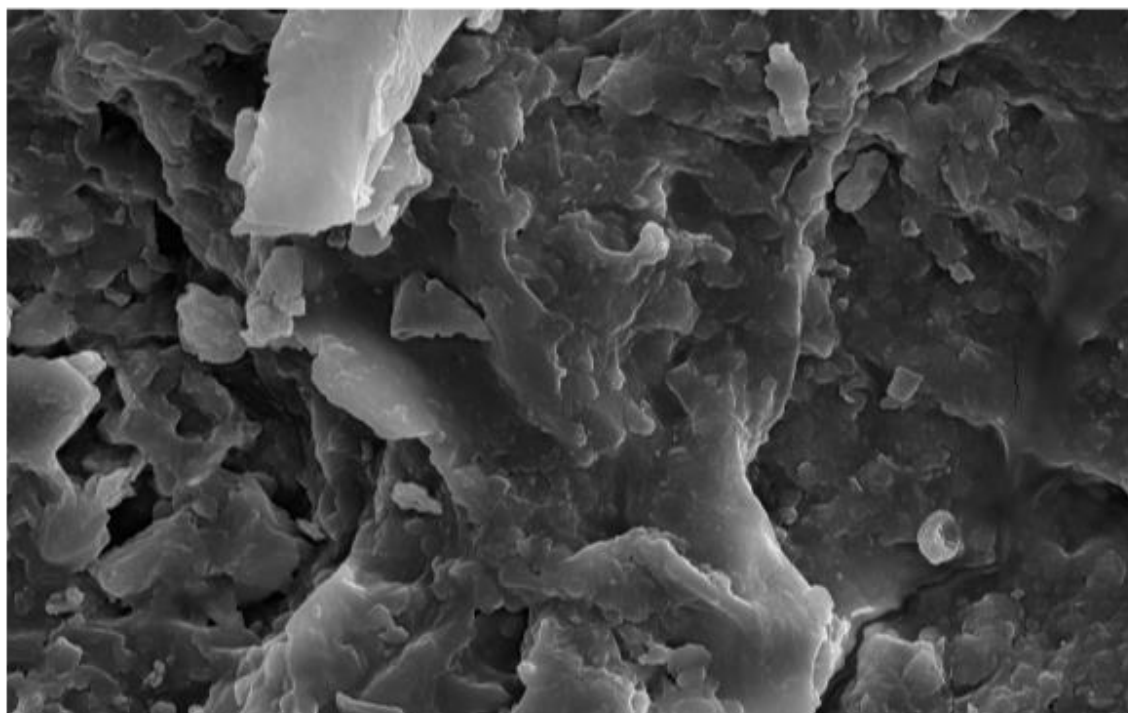


Figure 14: EDS spectra of GZ-B

Electron Image 1



10µm

Figure 15: SEM image of GZ-C

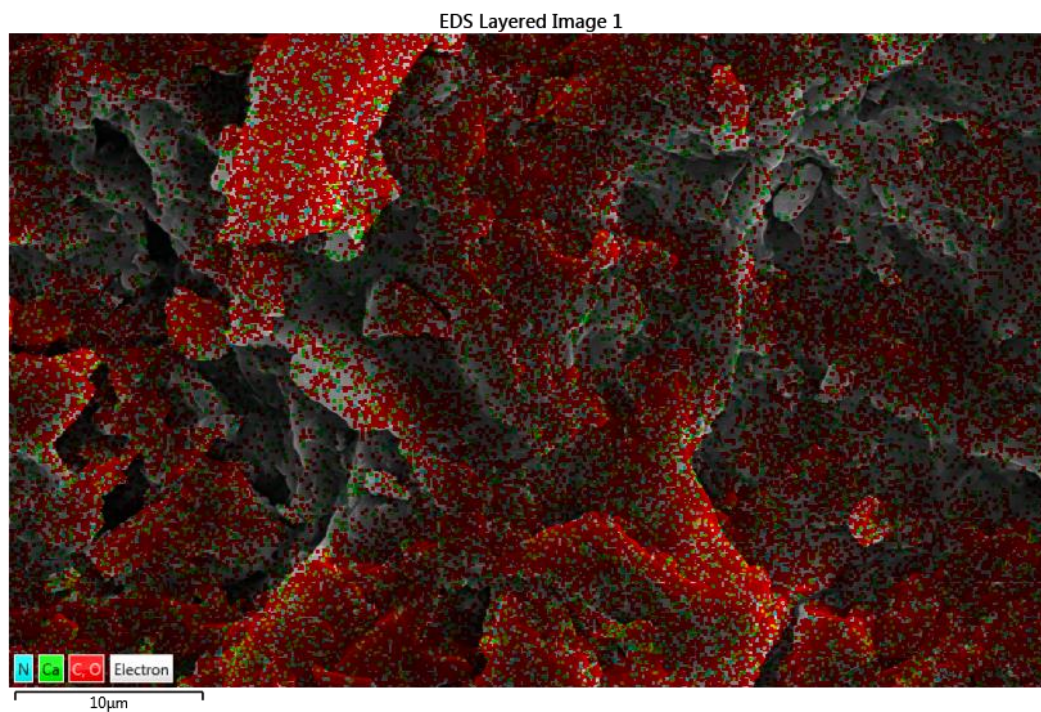


Figure 16: SEM/EDS Elemental mapping of GZ-C

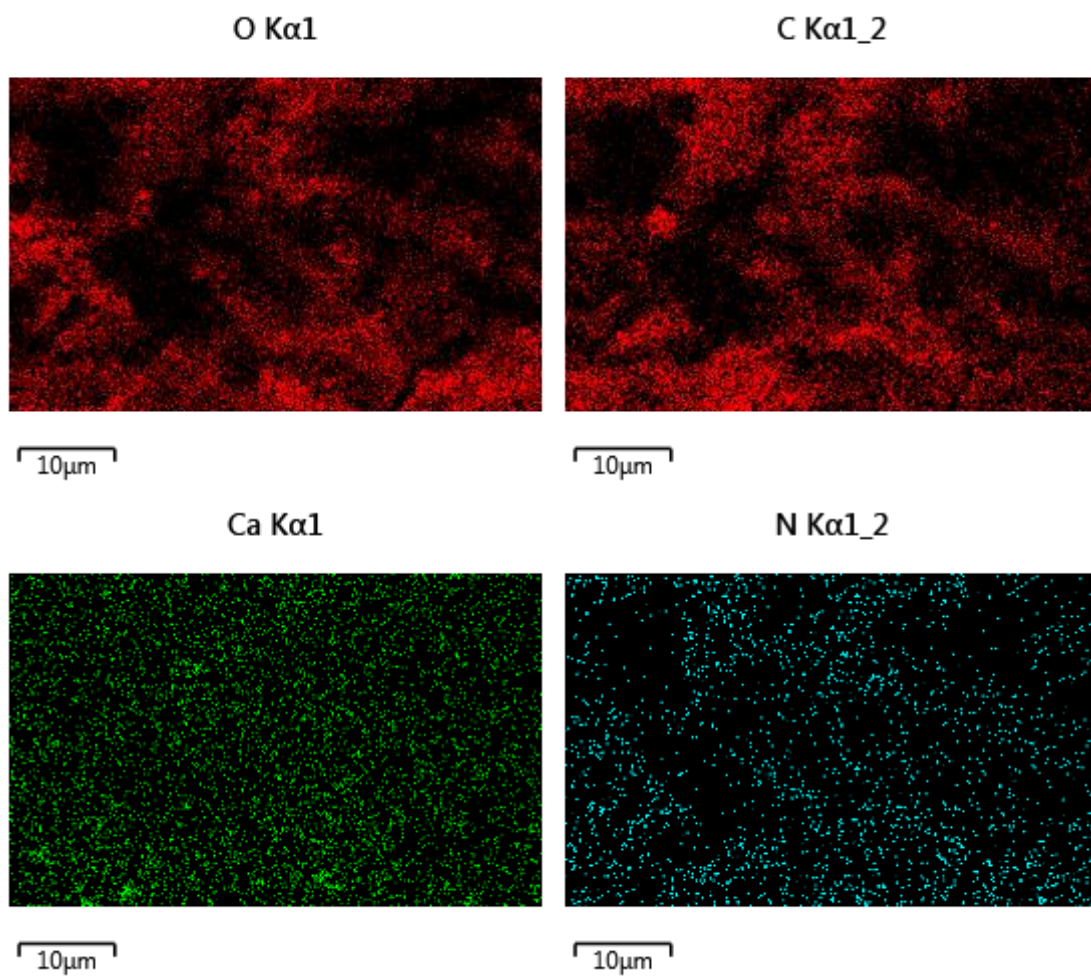


Figure 17: EDS mapping of GZ-C

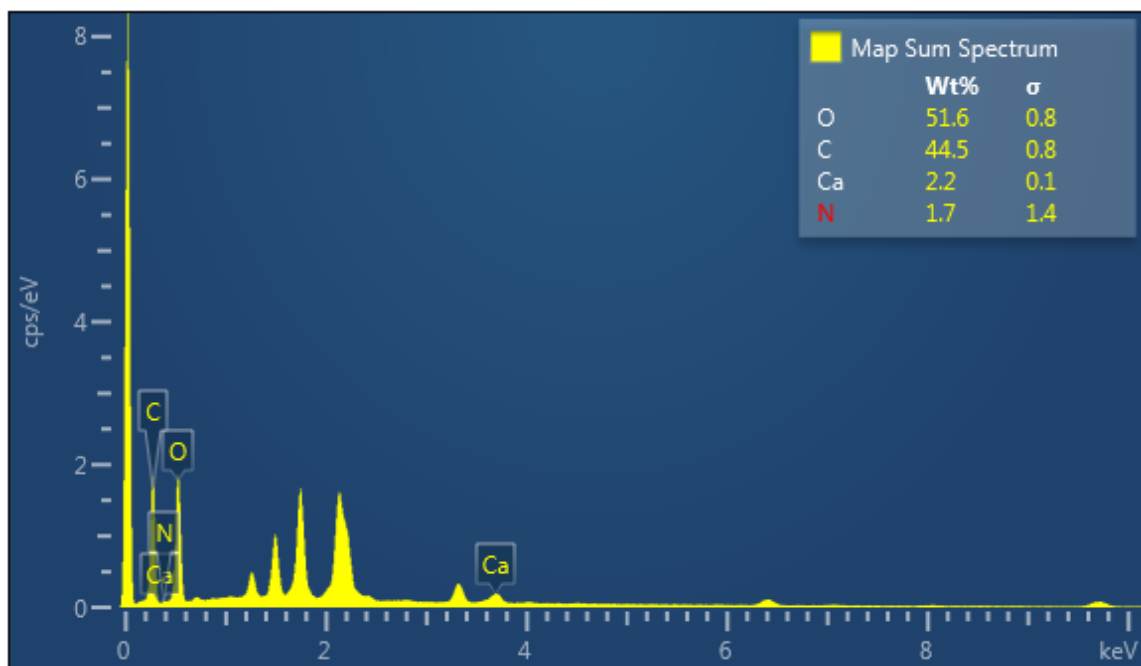


Figure 18: EDS spectra of GZ-C

Electron Image 1

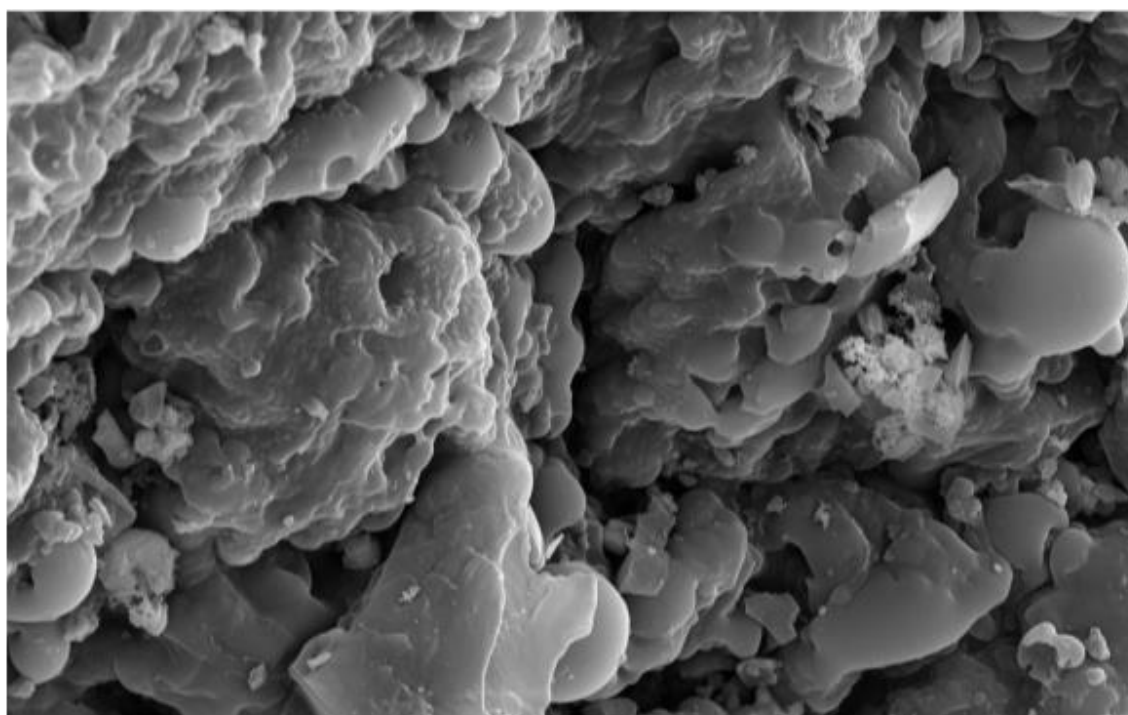


Figure 19: SEM image of GZ-D

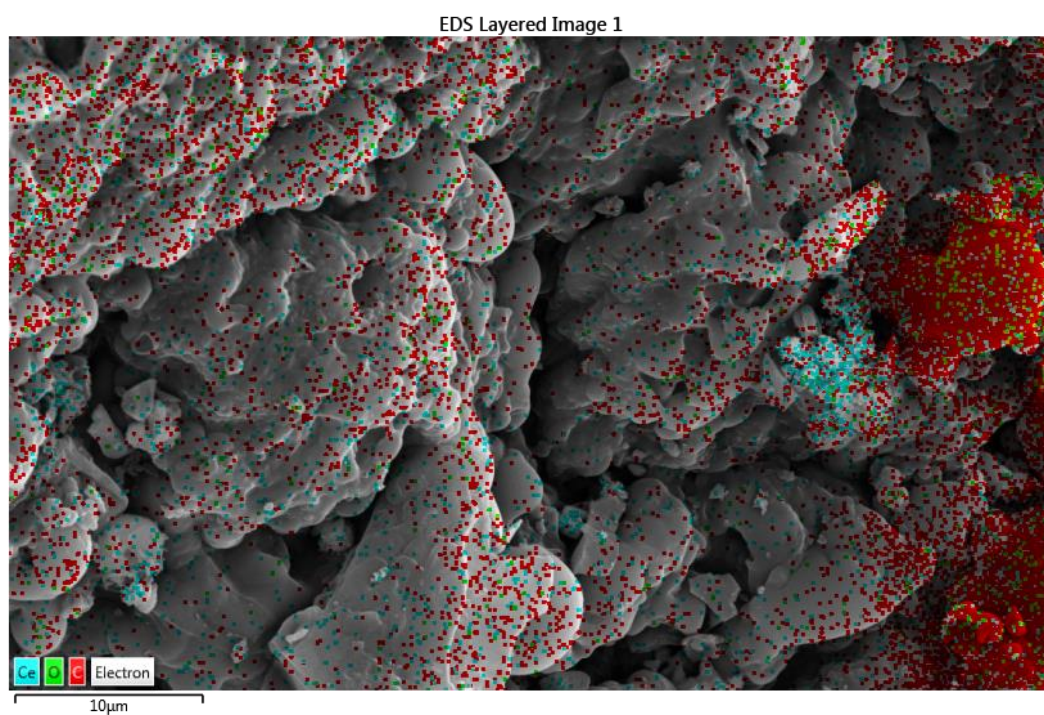


Figure 20: SEM/EDS Elemental mapping of GZ-D

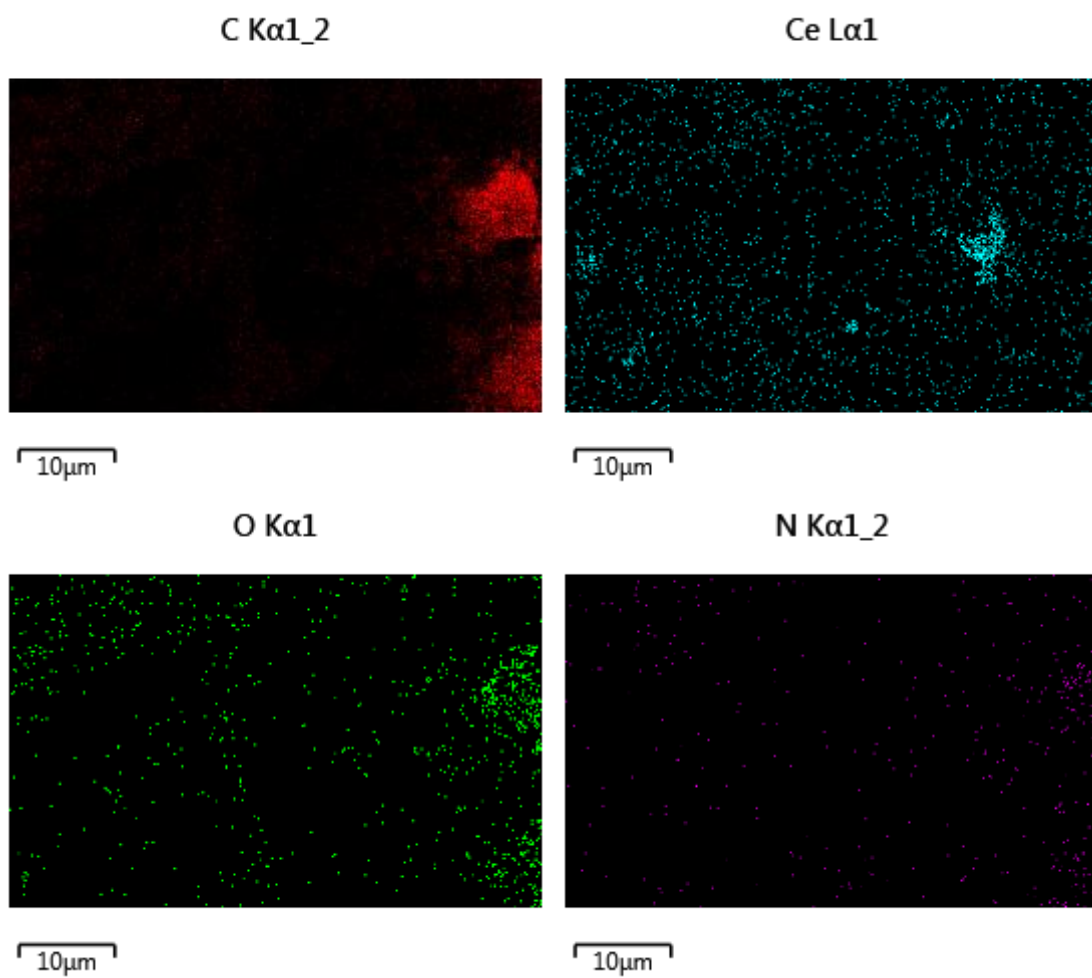


Figure 21: EDS mapping of GZ-D

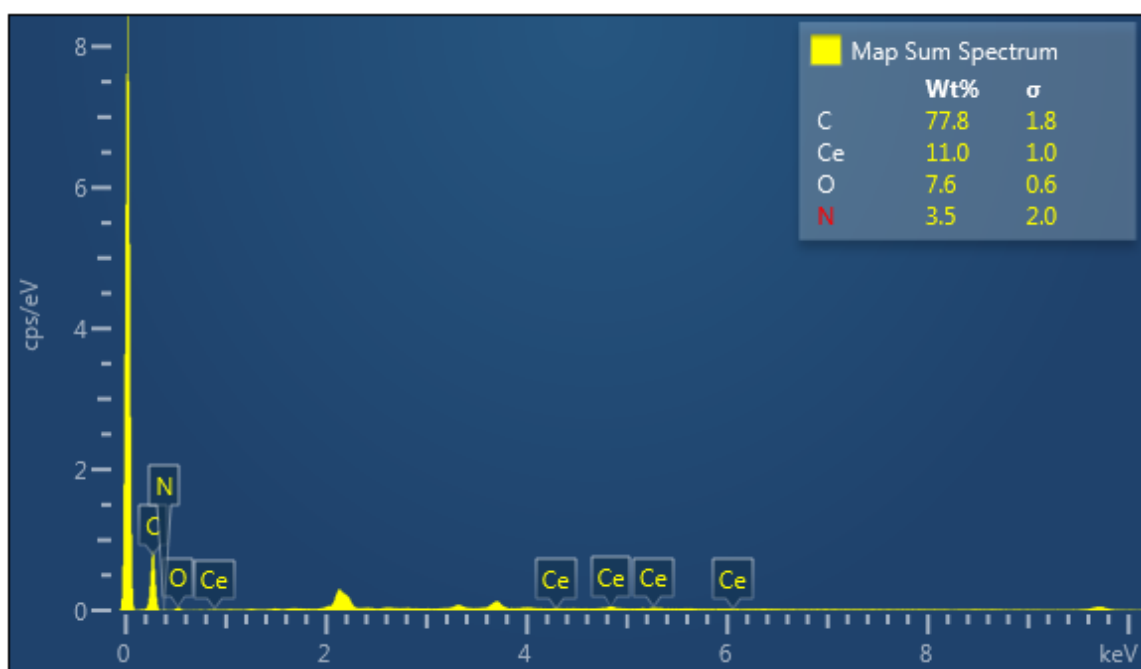


Figure 22: EDS spectra of GZ-D

Electron Image 1

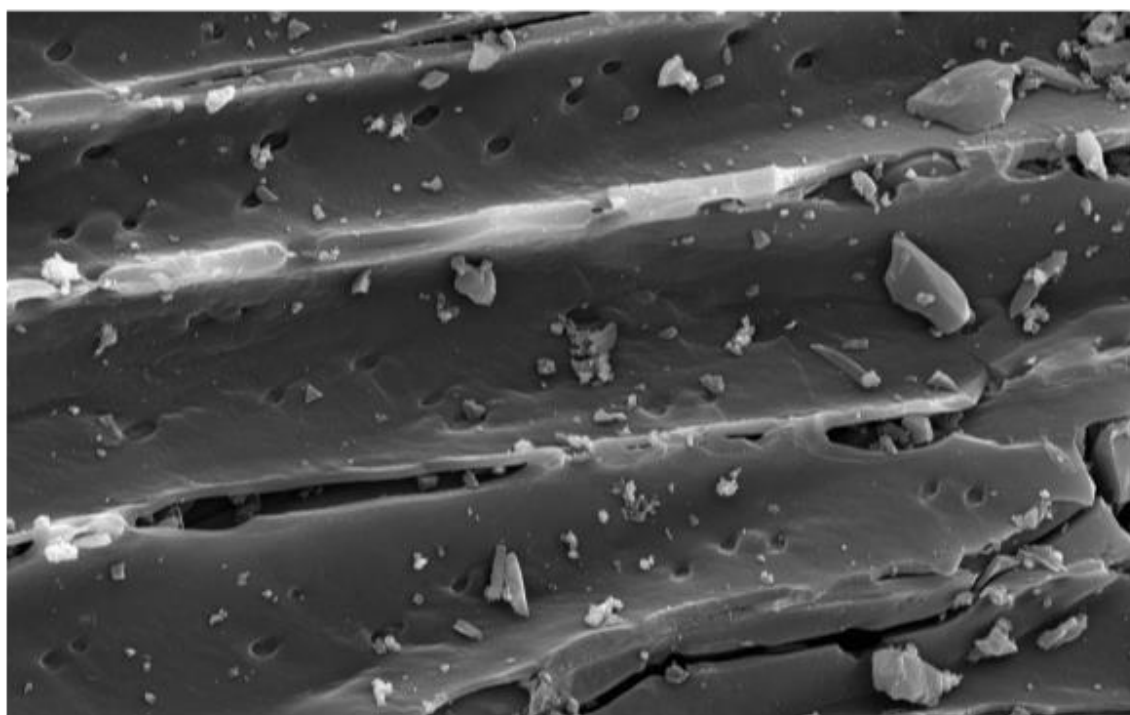


Figure 23: SEM image of GZ-E

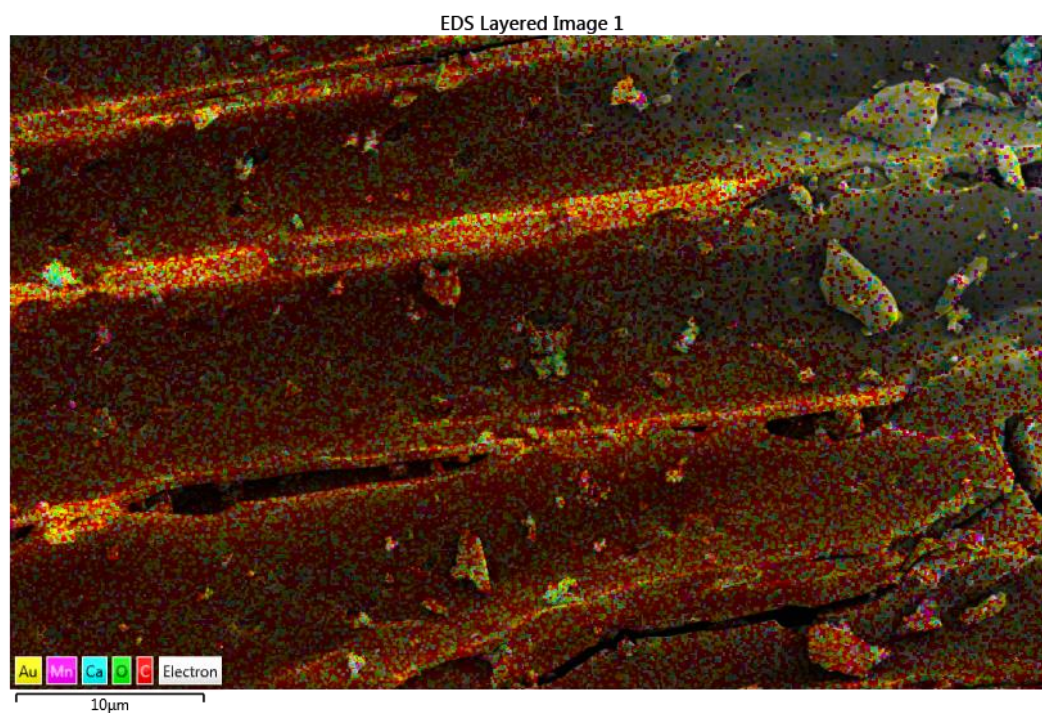


Figure 24: SEM/EDS Elemental mapping of GZ-E

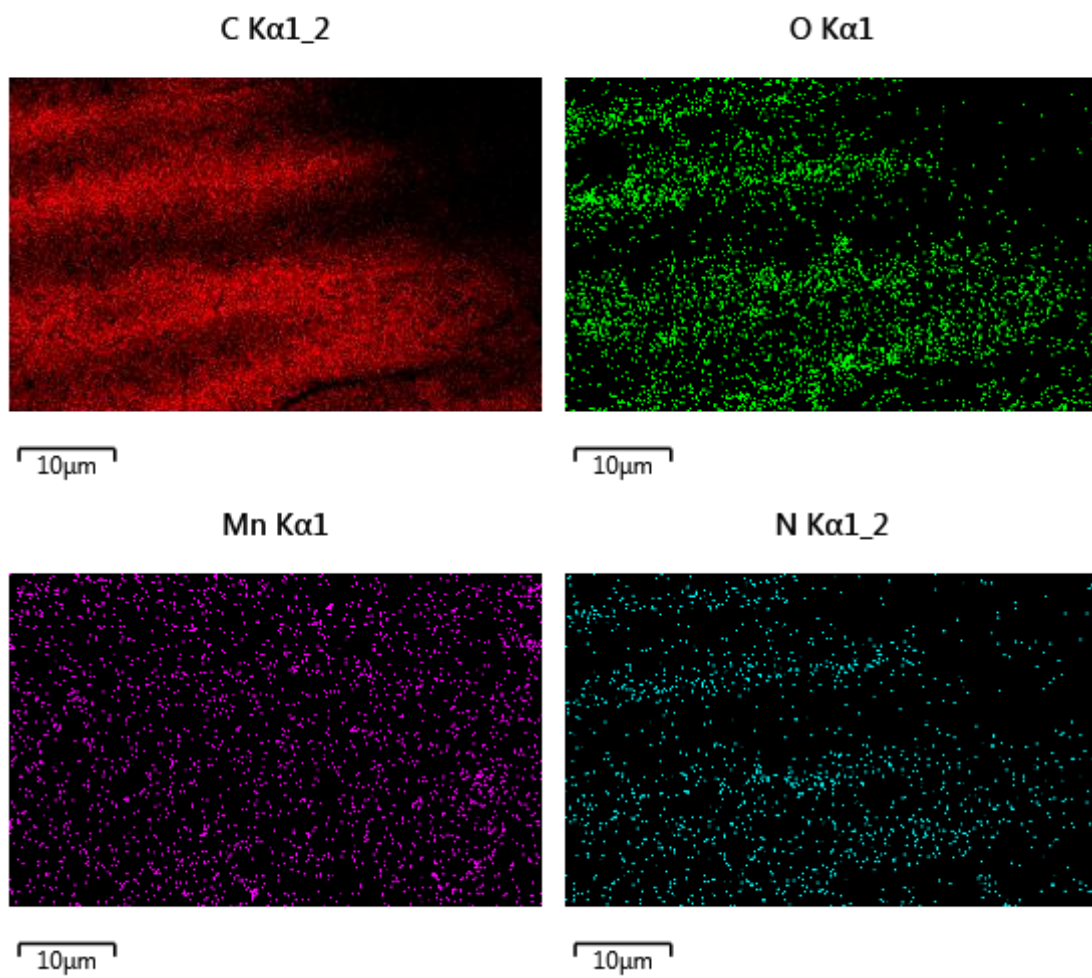


Figure 25: EDS mapping of GZ-E

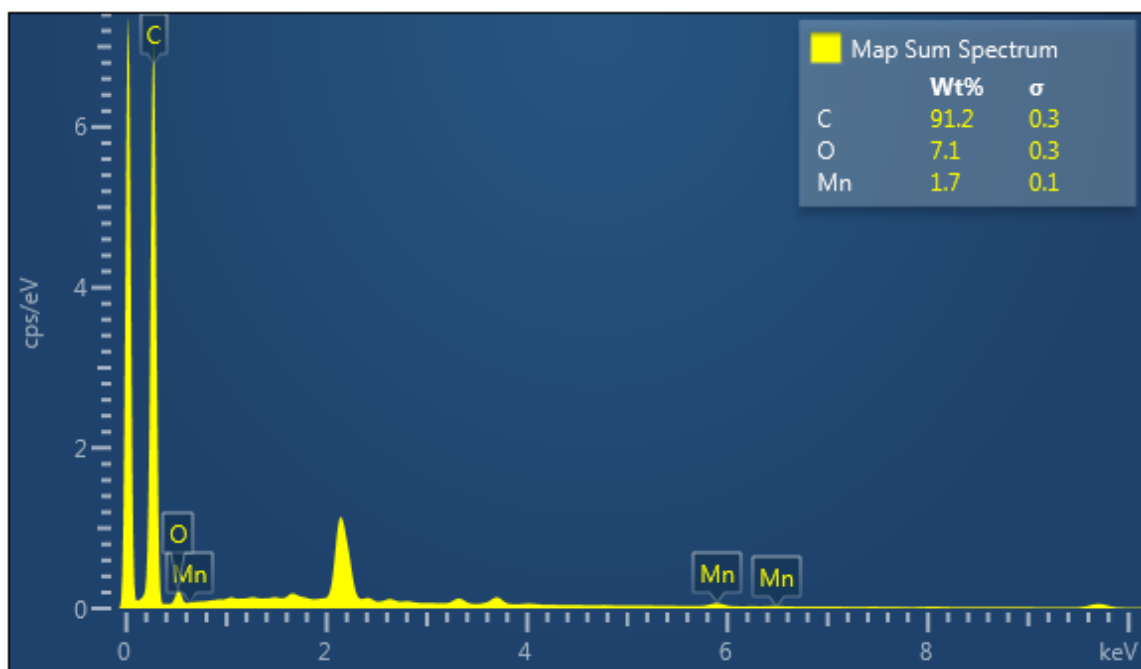


Figure 26: EDS spectra of GZ-E

4.6 Performance of Adsorbents for CO₂ Uptake

Following the surface area features observed for both primary and derived materials; GZ-A, GZ-B, GZ-C, GZ-D and GZ-E, the temperature dependent CO₂ adsorption was investigated. Meanwhile it is important to relay the fact that adopted Nitrogen-doped activated carbon emanated from the one of ratio 1:2 melamine respectively due to its high BET surface area.

Firstly, Nitrogen-doped activated carbon prepared at different activation temperatures of 600°C, 700°C, 800°C and 900°C were all subjected to CO₂ adsorption at 25°C and 40°C in order to determine and ascertain the best and optimum working temperature that will greatly enhance and to a very large extent support high CO₂ adsorption uptake. The result revealed that all the adsorbents prepared at different activation temperature demonstrated highest CO₂ adsorption uptake at an ambient temperature of 25°C compared to the other temperature with sample activated at 900°C having the highest uptake which eventually made sample activated at such temperature an optimum activation temperature. The figures below represent the plots of CO₂ adsorption at both temperature of 25°C and 40°C for samples prepared at activation temperature of 600°C, 700°C, 800°C and 900°C with their respective uptake represented in Table 3

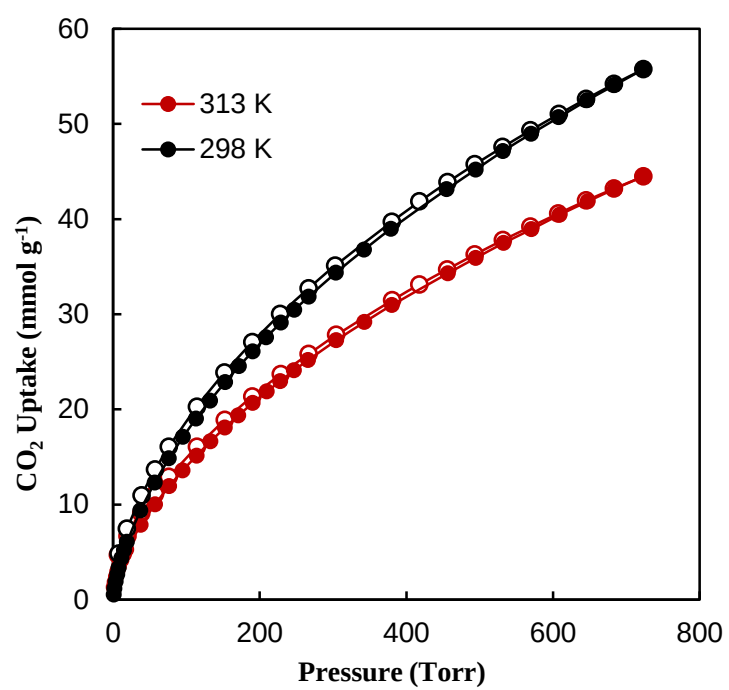


Figure 27: Activation temperature of GZ-B @ 600°C

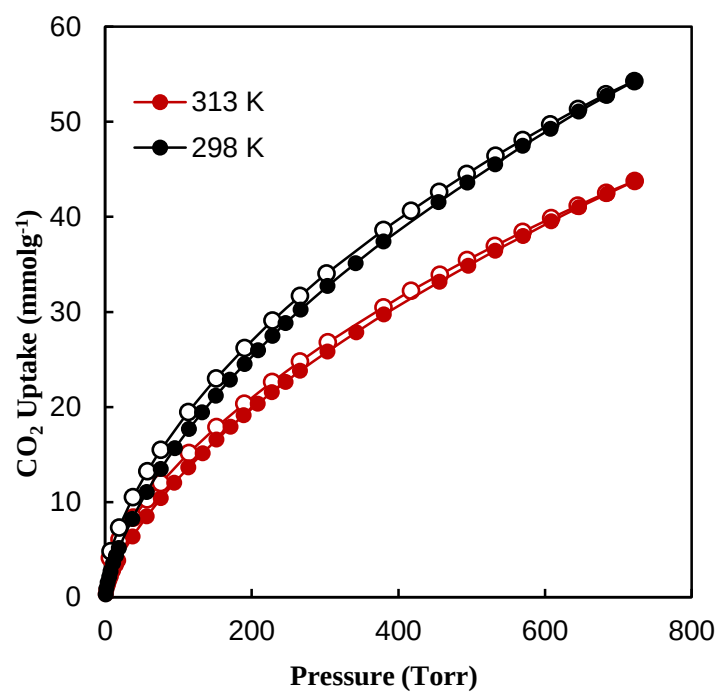


Figure 28: Activation temperature of GZ-B @ 700°C

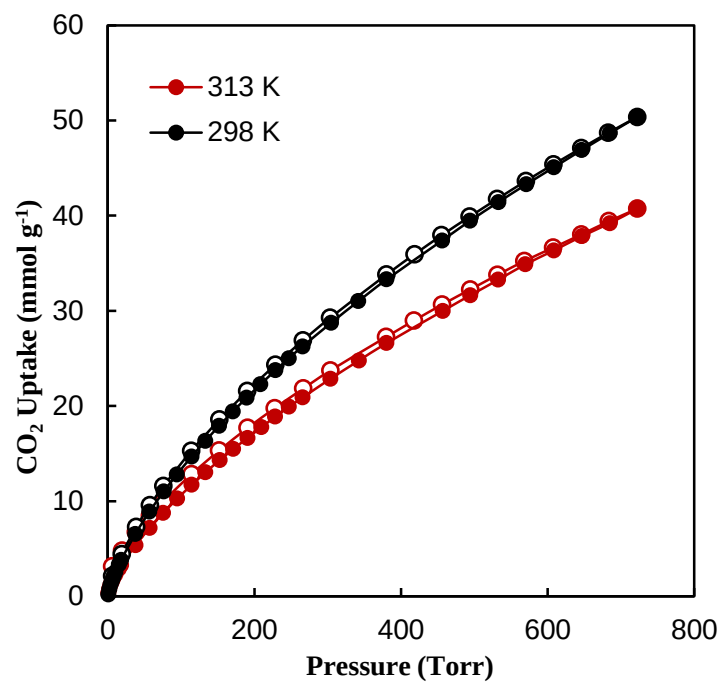


Figure 29: Activation temperature of GZ-B @ 800°C

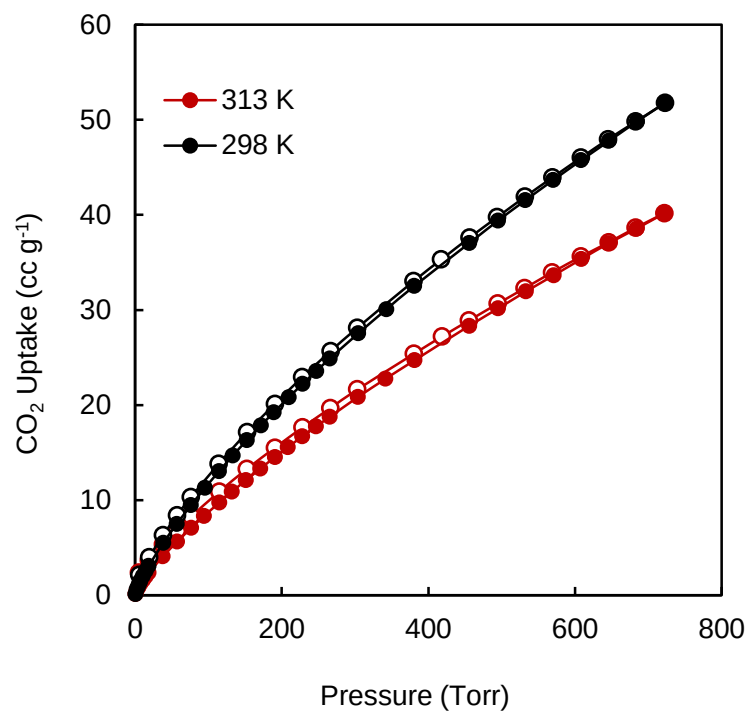


Figure 30: Activation temperature of GZ-B @ 900°C

Table 2 CO₂ Uptake of GZ-B @ different activating temperatures

Activated Temperature (Celsius)	CO ₂ (mmol/g) @ 25°C	CO ₂ (mmol/g) @ 40°C
600	2.49	1.98
700	2.42	1.95
800	2.24	1.82
900	3.43	1.79

Secondly, since the optimum activation temperature has been established, the primary sorbents alongside its derivative were all subjected to CO₂ adsorption at the same ambient working temperature of 25°C for all samples to further reaffirm its viability and applicability at ambient temperature. The result revealed that the CO₂ uptake is higher at ambient temperature comparatively for all materials with GZ-C having the highest uptake. Fig. 35 shows the comparative plot of CO₂ adsorption capacity at temperature of 25°C with adsorption efficiency depicted by Table 4. While some of the derived adsorbents show substantial higher adsorption capacity, while on the other hands, others are comparatively lesser to the primary pristine material. The enhanced advantage showed by some of these materials especially GZ-C could be aptly connected to a succinct interaction that exists between the amine group on the derived adsorbent and CO₂. [56, 57, 58, 59]. To explain this observation, many researchers have tendered dozens of explanation to elaborate this phenomenon. Also according to Vidal et al [60, 61], he explained this to have resulted from interaction using Nitrogen-doped nanohoops, where the CO₂ interactions increase with increase in number of Nitrogen atoms (that generate increased electron density). It is also of monumental importance to note that while surface area and pore volume are essential parameters in CO₂ adsorption capacity, it may however be misleading to solely depend on the value of the sorbent's surface area. GZ-C is a typical case study, it bears the highest CO₂ adsorption uptake of 3.56mmol/g with the smallest surface area compared to the pristine activated carbon.

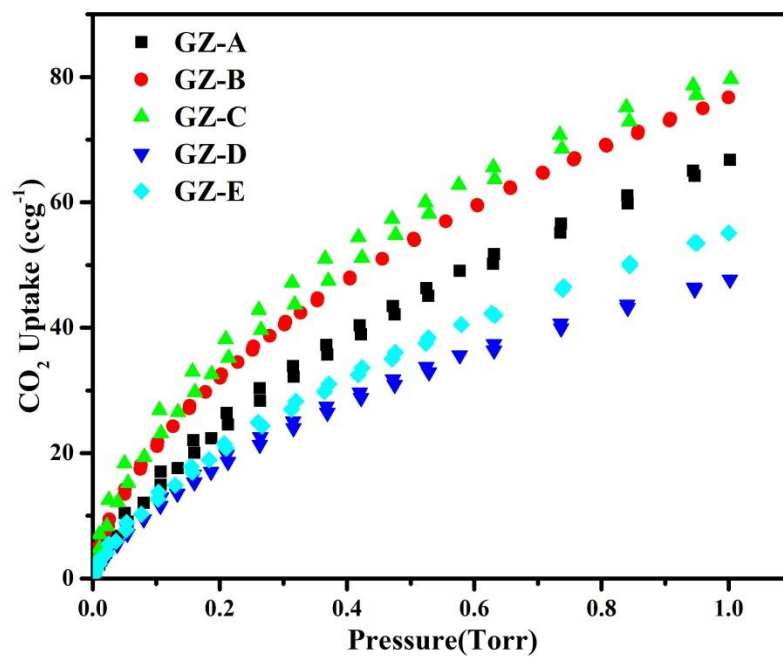


Figure 31: CO₂ Adsorption Uptake for various adsorbe

Table 3 : CO₂ Uptake and BET Surface area of Adsorbents.

Sorbent	A _{BET} (m ² /g)	CO ₂ Uptake (mmol g ⁻¹)
GZ-A	1184	2.78
GZ-B	1088	3.43
GZ-C	807	3.56
GZ-D	1026	2.13
GZ-E	1125	2.46

4.7 Selectivity of Adsorbents to CO₂ in the presence of Methane

In a bid to verify the efficiency of the primary and derived adsorbents to CO₂ adsorption in the presence of other gases, Methane was chosen to investigate the dual and selective ability of the adsorbents. The choice of Methane was born out of the fact that it is one of the greenhouse gases with high potential of trapping high amount of heat thereby causing an adverse effect on the temperature of the globe. To ascertain this, the effect of the presence of CH₄ in the adsorption strength of the materials to CO₂ adsorption was investigated under the same experimental conditions of 298K and 760 Torr. As shown in Fig. 36 GZ-C exhibit higher CO₂ adsorption uptake when compared to CH₄ uptake which is a strong indication of enhanced interaction between Nitrogen and CO₂. This shows that this material has a good potential in adsorbing CO₂ from flue gas. Also the CO₂ uptake shown at ambient temperature by some of these derived materials can compete favorably with some of the existing and highly ranked adsorbents, Table 6 depicts this fact. In addition to these essential attributes coupled with its nature of being readily available will inadvertently afford it an edge for CO₂ adsorption.

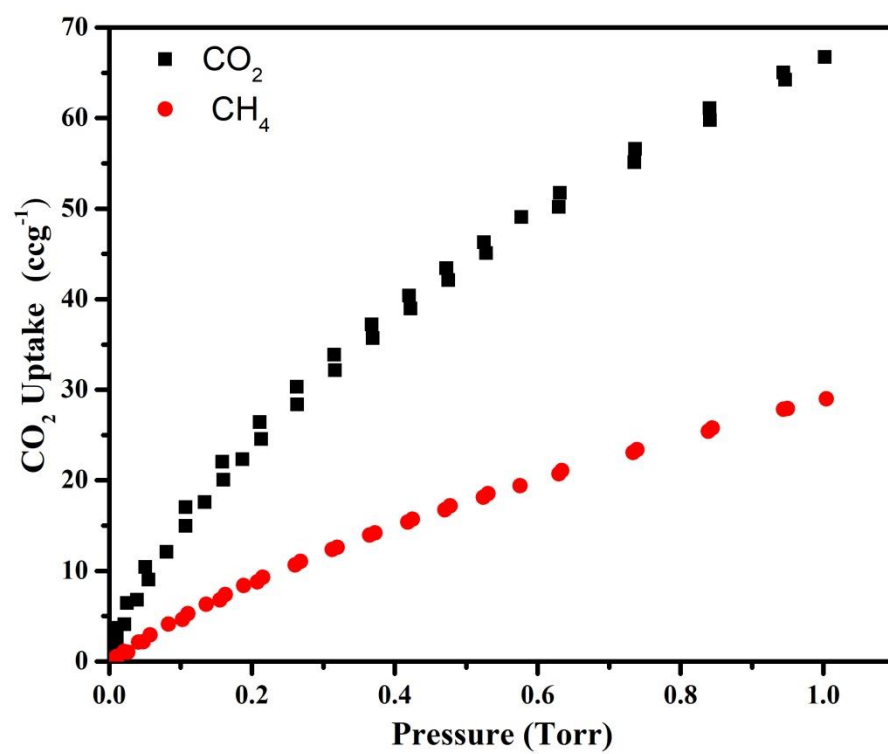


Figure 32: Selectivity plot of GZ-A for CO₂ Adsorption in the presence of CH₄

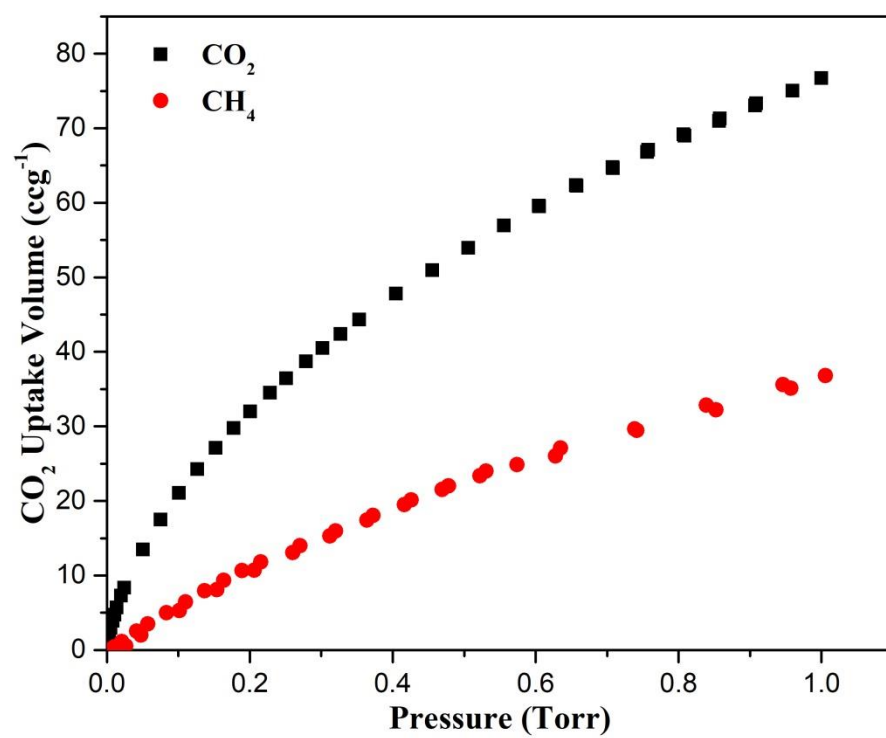


Figure 33: Selectivity plot of GZ-B for CO₂ Adsorption in the presence of CH₄

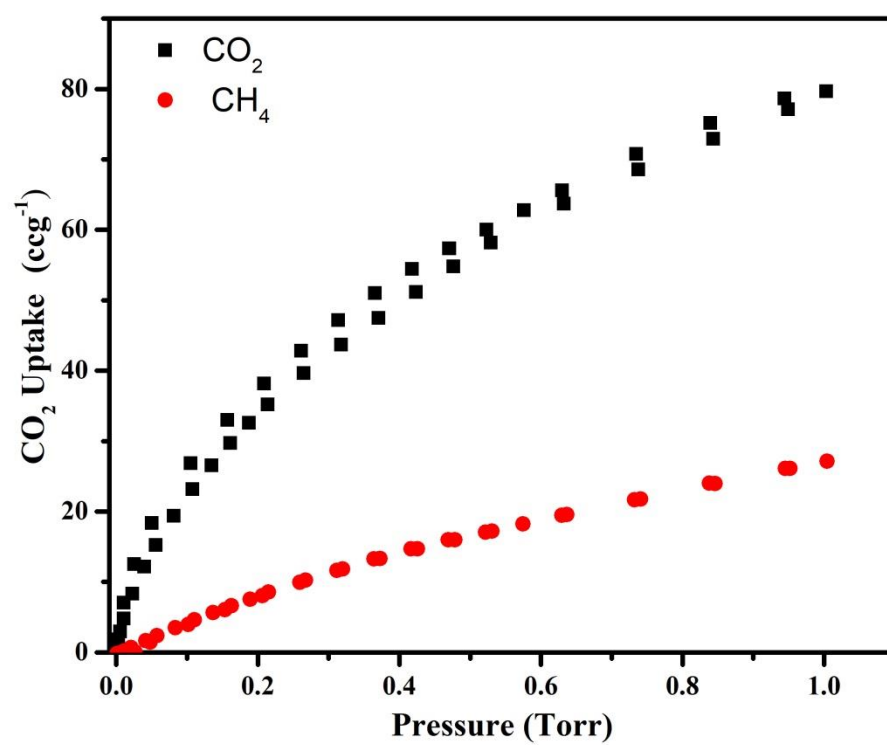


Figure 34: Selectivity plot of GZ-C for CO₂ Adsorption in the presence of CH₄

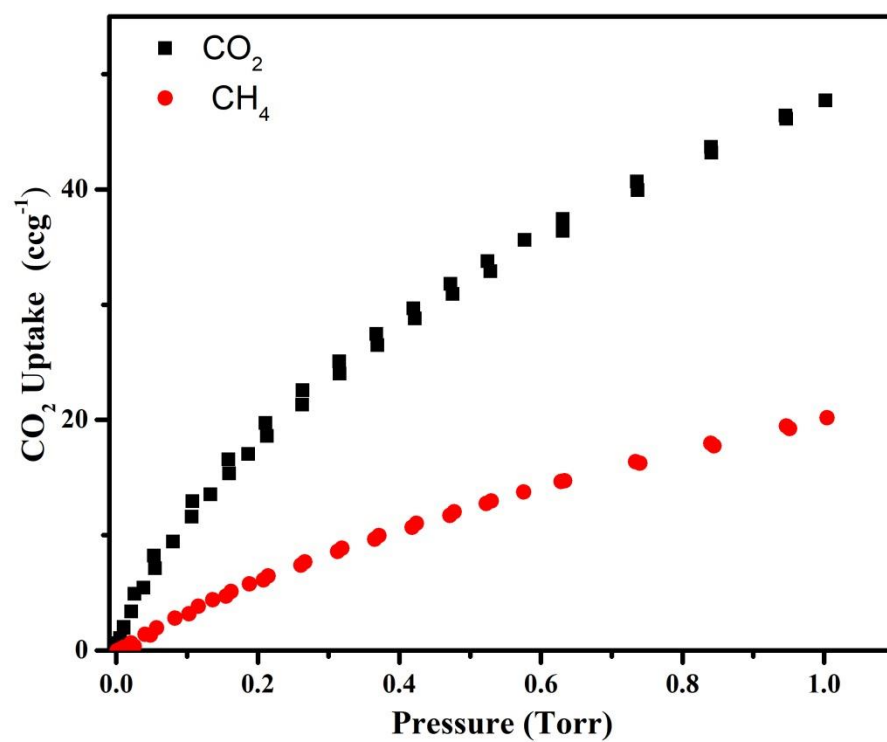


Figure 35: Selectivity plot of GZ-D for CO₂ Adsorption in the presence of CH₄

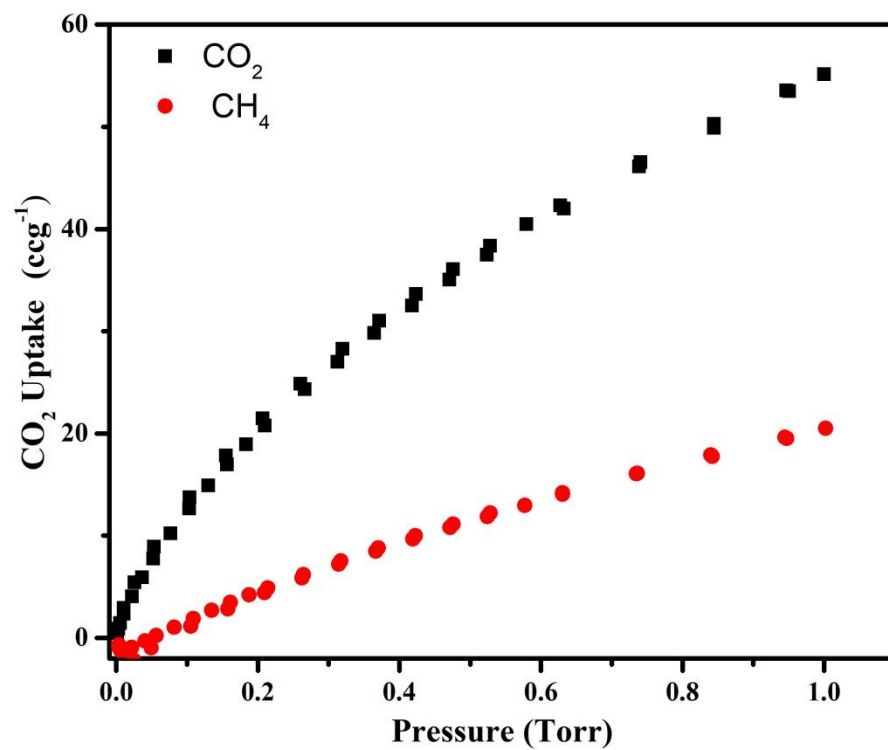


Figure 36: Selectivity plot of GZ-E for CO₂ Adsorption in the presence of CH₄

Table 4: Adsorbents selectivity to CO₂ in the presence of CH₄

Adsorbents	CO ₂	CH ₄
	Uptake	Uptake
	(mmol/g)	(mmol/g)
	@ 25°C	@ 25°C
GZ-A	66.76	28.97
GZ-B	76.73	36.80
GZ-C	79.67	27.12
GZ-D	47.71	20.19
GZ-E	55.13	20.52

Table 5: Comparison of the CO₂ adsorption efficiency of different materials.

Materials	T(k)	P(bar)	CO ₂ Uptake (mmol g ⁻¹)	Ref
P-g-C ₃ N ₄	298	1	0.39	[62]
MCM-41-NH ₂	308	2.5	1.20	[63]
MCN/C	298	1	2.35	[64]
a-MCN	298	1	2.69	[65]
Hierarchical PCN	298	1	2.90	[66]
A2-BPMO	298	1.2	3.03	[67]
PS	313	1	3.63	[67]
SG-CN(2)	298	1	3.34	[69]
GZ-B	298	1	3.43	This work
GZ-C	298	1	3.56	This work

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

To summarize, series of CO₂ adsorbents (both pristine and derived) were synthesized from cost-friendly and highly abundant carbon precursor (groundnut shell) with melamine as the nitrogen source which was later impregnated with specific metals namely Cerium (Ce), Calcium (Ca) and Manganese (Mn) to enhance CO₂ capture. The derived adsorbents were all characterized using FTIR, RAMAN, BET, SEM, and XRD.

Firstly, the aftermath effect of heightened functionalization of amine on the adsorbents' properties and CO₂ uptake was also investigated. The result revealed that all the nitrogen-doped materials (1:1, 1:2 and 1:3) show enhanced CO₂ uptake compared to the pristine activated carbon. Supposedly, the functionalization or amine has contributed immensely to the enhancement in the adsorption capacity due to the intimate interaction between nitrogen and CO₂. Furthermore, of all the nitrogen-modified adsorbents, an adsorbent with intermediate nitrogen content demonstrated maximum surface area and micropore volume and consequently highest CO₂ uptake.

Secondly, to probe further the enhancement of CO₂ uptake, the optimum nitrogen-modified adsorbent was impregnated with various metals Ce, Ca, and Mn at different loading weight of 1%, 2% and 5% for each metal. While the result of 1% and 2% loaded weight are still being awaited for all the metals, 5% Ce, on the other hand, demonstrated top-notch CO₂ uptake compared to all the nitrogen-doped adsorbents as well as 5% of all two other metals. This striking enhancement effect may be related to the metal-adsorbent interaction.

5.2 Recommendation

To fully maximize the viability and applicability of these adsorbents, a detailed comparison of differently impregnated metal-loaded (1%, 2% and 5%) weight should be thoroughly investigated; furthermore, the chemistry of the effect of nitrogen functionalization on carbon and its function in CO₂ uptake and enhancement should be investigated accordingly with the aid of DFT calculations.

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