

Characterization and Emission Control Potential of Shell-Based Sorbents in Internal Combustion Engine Exhaust System

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Abstract—Despite the enactment of the Philippine Clean Air Act over thirty years ago, effective control of air pollution remains a persistent challenge, particularly from vehicular emissions, which account for 20–35% of air pollutants. This study aims to explore sustainable alternatives for capturing vehicular emission pollutants using calcium oxide (CaO) derived from waste materials such as oyster shells, mussel shells, and chicken eggshells. These biomaterials were analyzed to determine their potential as low-cost and eco-friendly sorbents. X-Ray Fluorescence (XRF) was used to assess elemental composition, Fourier Transformed Infrared Spectroscopy (FTIR) to identify functional groups, and Thermo-Gravimetric Analysis (TGA) to evaluate thermal stability under simulated exhaust conditions. Results revealed that all samples contained high levels of calcium carbonate (CaCO₃), with mussel shells having the highest calcium concentration (38.371%). FTIR confirmed the presence of CaCO₃ functional groups, while TGA showed favorable thermal decomposition properties, particularly in mussel shells, which began decomposing above 600°C. The presence of hydroxyl compounds in mussel shells further suggests enhanced adsorption capabilities. Overall, mussel shells emerged as the most promising material for emission pollutant capture, but further testing in real-world conditions is recommended to validate their practical application in environmental pollution control systems.

Keywords—Calcium Carbonate, Elemental Composition, Emission Pollutant, Functional Group, Material Characterization, Thermal Stability, Waste Shells

I. INTRODUCTION

In the Philippines, despite the enactment of the Clean Air Act three decades ago, comprehensive air pollution control remains elusive. Recent studies reveal that PM_{2.5} concentrations in urban areas surpass the World Health Organization's recommended guidelines, with notable implications for public health [1]. The Western Pacific region, including the Philippines, exhibits the highest PM_{2.5}-attributable mortality globally. Motor vehicles contribute significantly to this air pollution crisis, accounting for half of total CO₂ emissions and substantial proportions of hydrocarbon and NO_x emissions. Vehicular emissions are projected to double if current trends persist, making them a critical concern for air quality.

Diesel and gasoline, commonly used for their energy efficiency, pose environmental challenges due to the release of air pollutants and greenhouse gases. Recent estimates in the Philippines for 2008 indicate CO₂ emissions of 30 million tons and 56 thousand tons of particulate matter, with 38 percent originating from the transport sector's fuel combustion. If current trends persist, motorized vehicles and air pollutants are anticipated to double under the business-as-usual scenario. Presently, vehicular emission is the most dominant source of air pollutants, comprising 20–35% only in Metro Manila [2]. To address these environmental issues, this study investigates the potential of alkaline earth metal oxides, specifically calcium oxide (CaO), sourced from sustainable outlets like discarded seashells (oyster and mussels) and eggshells. These materials present a cost-efficient and environmentally friendly alternative to nonrenewable options like dolomite and limestone, which cause ecological damage during extraction. The research concentrates on seashells (oyster and mussels) and eggshells due to their abundant availability as biomaterials and their natural decomposition process. Through the characterization of these shells and an assessment of their efficacy in capturing CO₂ and other emission pollutants, the study aims to provide valuable insights into sustainable approaches for addressing air pollution stemming from vehicular emissions in the Philippines.

A. Objectives

The primary aim of this research is to analyze and characterize oyster, mussel, and chicken egg shells to assess their suitability for carbon capture and storage applications in engines. To accomplish this goal, the study will employ the following analysis:

1. X-Ray Fluorescence Analysis:
 - 1.1 Determine the elemental composition of the shells.
 - 1.2 Identify the presence of elements that might enhance or hinder pollutant adsorption capacities.
2. Fourier Transformed Infrared Spectroscopy:
 - 2.1 Identify the functional groups present on the shell's surface, focusing on those with potential affinity for different pollutant types.
3. Thermo-Gravimetric Analysis:
 - 3.1 Assess the thermal stability of the shells under simulated exhaust temperatures.
4. Determine which shell has the most potential for emission pollutant capture

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II. METHODS

The methodology adopted in this study is designed to thoroughly evaluate oyster, mussel, and chicken eggshells as potential absorbents for emission pollutants. Using a systematic and multidisciplinary approach, the research explores the structural, chemical, and physical characteristics of these natural materials to assess their effectiveness in reducing environmental pollution. A variety of analytical techniques, including spectroscopy, microscopy, and chemical assays, will be used to examine the key properties that influence their ability to absorb pollutants. This detailed analysis aims to provide valuable insights into the potential use of these waste materials as sustainable and cost-effective solutions for pollutant capture and environmental protection.

A. Flow of the Study

The research methodology covers through a structured progression comprising two distinct phases: preparation and characterization. This methodical and systematic flow is designed to provide a comprehensive understanding of the investigated processes, each phase contributing significantly to the achievement of research objectives.

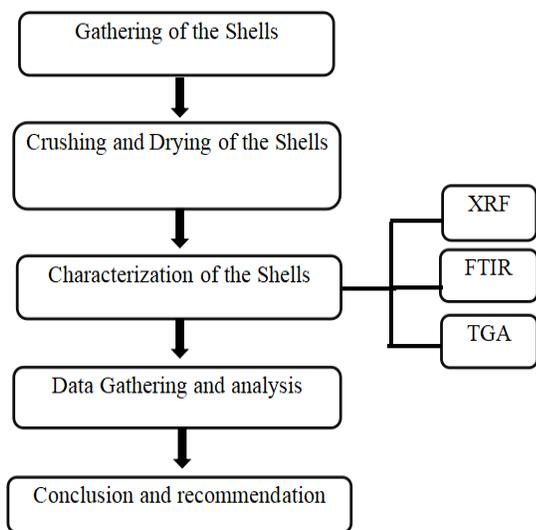


Fig. 2-1. The Flow of the Study

B. Research Design

This study adopts a quantitative approach and applies a descriptive research design to thoroughly examine the chemical characteristics of oyster, mussel, and chicken eggshells in relation to their potential for capturing emission pollutants. X Ray Fluorescence (XRF) analysis is used to determine the elemental composition of the shells, focusing on elements relevant to pollutant absorption. Fourier Transform Infrared Spectroscopy (FTIR) identifies functional groups present on the shell surface, particularly those associated with contaminant binding. In addition, Thermogravimetric Analysis (TGA) assesses the thermal stability of the shells across a range of temperatures. Through this combined quantitative and descriptive approach, the study provides a detailed

understanding of the composition and properties of oyster, mussel, and chicken eggshells, highlighting their potential as effective materials for emission pollutant capture.

C. Research Instruments

In this study, the characterization of oyster, mussel and chicken eggshell will be conducted using advanced analytical tools. X-Ray Fluorescence Analysis (XRF) will be employed to analyze the elemental composition of a material by measuring the X-rays emitted when the sample is bombarded with high-energy X-rays. It identifies and quantifies the elements present in the sample, typically down to parts per million (ppm) levels. Fourier Transform Infrared Spectroscopy (FTIR) will play a crucial role in the analysis of functional groups and chemical bonds present in the shell, aiding in the identification of specific molecular vibrations. Additionally, Thermogravimetric Analysis (TGA) will be an instrument in studying the material's thermal stability and decomposition behavior, offering crucial information on weight changes in response to varying temperatures of the engine. On the other hand, there will be a use of a drying oven to ensure controlled and uniform drying of samples, eliminating any moisture or volatile components before analysis.

Collectively, these advanced analytical instruments contribute to a thorough understanding of the material's structural, chemical, and thermal properties. This comprehensive characterization is integral for evaluating the material's suitability for sustainable emission pollutant capture and its potential applications in exhaust systems.

D. Gathering and Preparation of Oyster Shells

In the preliminary phase of the study, oyster, mussel and chicken egg shells will be gathered from a designated source and systematically prepared. This process involves cleaning, drying, and other necessary treatments to ensure the shells are ready for subsequent analysis, establishing the groundwork for an in-depth exploration of their potential as a emission pollutant absorbent.

2.4.1. Collection of Oyster Shells

The oyster, mussel and chicken egg shells will be collected in Libo, Tayud, Consolacion, Cebu, a region recognized for having a significant number of seashell farms, especially based on available statistics. Consolacion, in particular, stands out as a prominent hub for seashell cultivation in the northern part of Cebu. The selection of this location is intentional, aiming to conduct a comprehensive study on local seashells.

2.4.2. Crushing

The shells will undergo a crushing process, breaking them into small particles. This step is crucial to ensure a uniform firing area for the subsequent phase. Additionally, the crushing process will effectively eliminate foreign materials such as epibionts, seaweeds, and sediments, enhancing the purity and consistency of the shell particles. This preparation is essential to optimize the conditions for the upcoming analyzation of specimen.

2.4.3. Drying

The oyster, mussel and chicken egg shells will undergo a two-step drying process to enhance their suitability for the study. Initially, they will be exposed to sunlight for 24 hours to eliminate external moisture and reduce internal moisture content. Following this, the shells will be subjected to a drying oven set at 150 degrees Celsius for an additional 24 hours. This step will serve the dual purpose of further removing any remaining moisture and ensuring the elimination of potential pathogens, bacteria, and other microorganisms that might influence the results.

2.4.4. Sieving

Following the drying process, a precise sieving technique will be applied to the shells, specifically targeting a particle size of 75 micrometers. This operation aims to selectively separate particles, ensuring a uniform size range for further analysis and providing essential insights into the oyster shells' characteristics and suitability as an adsorbent.

E. Characterization of Oyster, Mussel and Chicken egg Shells

The characterization of oyster, mussel and chicken egg shells involves examination of their structural, chemical, and physical properties to inform the subsequent stages of experimentation and optimize their potential as an adsorbent.

2.5.1. X-Ray Fluorescence Analysis

X-Ray Fluorescence Analysis will identify the types and concentrations of elements in the shells, especially those relevant to pollutant capture. It will also assess the presence and abundance of elements that can enhance or hinder pollutant adsorption capacities.

2.5.2. Fourier Transform Infrared Spectroscopy Analysis

This tool will analyze the functional groups present on the surface of the shells, focusing on those with potential affinity for different types of pollutants. Additionally, it explores the potential contribution of organic matter and its functional groups to pollutant capture, providing insights into the overall pollutant adsorption capacity.

2.5.3. Thermogravimetric Analysis

Thermogravimetric Analysis will evaluate the thermal stability of the shells under simulated exhaust temperatures, providing information on the material's ability to withstand conditions in engine exhaust systems. Moreover, it will identify the temperature range at which significant pollutant release occurs, helping to understand the potential application and limitations of oyster shells in capturing and storing pollutants.

These data form the basis for the analysis and interpretation, thereby accomplishing the objectives of this study.

A. Elemental Composition of the Shells

X-ray fluorescence spectroscopy (XRF) analysis was conducted to determine the composition of oyster shell, mussel shell, and chicken eggshell, with the aim of evaluating their potential as sources of calcium carbonate. Each value reported is the average of three measurements. Calcium carbonate, denoted by the chemical formula CaCO_3 , consists of three main elements: carbon, oxygen, and calcium. This compound is commonly found in rocks worldwide, particularly as limestone [91]. Calcium carbonate (CaCO_3) is effective as an adsorbent for air pollutants, particularly sulfur dioxide (SO_2) and nitrogen oxides (NO_x). This compound is used in processes like flue gas desulfurization, where it reacts with SO_2 to form calcium sulfite or sulfate, thereby reducing the emission of these harmful gases. Additionally, calcium carbonate can neutralize acidic pollutants, contributing to improved air quality and reduced acid rain formation [92]. Eggshells are rich in mineral salts, primarily consisting of calcium carbonate, which accounts for about 94% of the shell [93]. Oyster shells are also mainly composed of calcium carbonate (CaCO_3), approximately 96%, in the form of calcite and aragonite crystals [94]. Similarly, mussel shells are primarily made up of about 94% calcium carbonate [95]. The chemical composition of all three samples is predominantly calcium carbonate (CaCO_3), with some impurities.

Elemental content analysis was performed using Bruker S1 TITAN 800 Handheld X-Ray Fluorescence (HXRF) with XRF parameters listed in Table III.I.

TABLE III.I PARAMETERS USED FOR XRF ANALYSIS

Parameters	Parameter Type/ Value
Application	Geo Exploration (Auto)
Test total duration	90 seconds
Measurement units	% conc.
Replicates	3
Maximum voltage	50 keV

The summarized results of the XRF test for the samples (*Chicken Eggshell, Oyster, and Mussel*) are presented in *Tables III.II to III.IV*. The results displayed are averaged from three (3) measurements indicating the elemental concentrations and standard deviations in percent (% wt.). The spectra of the samples run at 30 kV and 50 kV are shown in *Figures 3.1 to 3.3*.

TABLE III.I SUMMARIZED XRF RESULTS FOR THE SAMPLE CHICKEN EGGSHELL

III. RESULTS AND DISCUSSION

To provide context regarding the elemental composition, functional groups, and thermal stability of the shells, data from various material testing techniques, including X-ray Fluorescence Analysis, Fourier Transform Infrared Spectroscopy, and Thermogravimetric Analysis, are provided.

Element		Conc. [% wt.]	Stddev [% wt.]
Calcium	Ca	35.253	0.083
Aluminum Oxide	Al ₂ O ₃	1.453	0.246
Sulfur	S	1.240	0.029
Chlorine	Cl	0.704	0.025
Potassium Oxide	K ₂ O	0.307	0.009
Strontium	Sr	0.058	0.001
Nickel	Ni	0.005	0.001
Copper	Cu	0.003	0.001

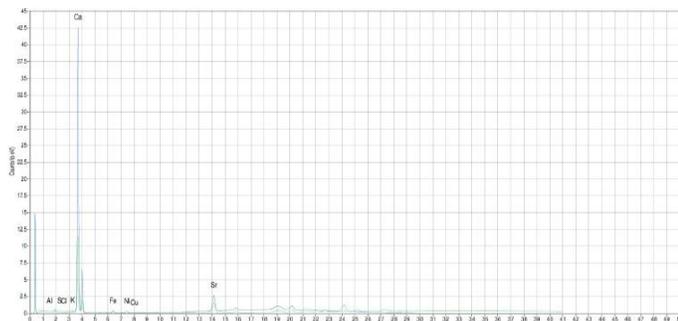


Fig. 3.1. XRF spectra of the sample Chicken Eggshell

For the Chicken Eggshell, the concentration percentages are: Calcium 35.253% with a standard deviation of 0.083%, Chlorine 0.704%, Sulfur 1.240%, Phosphorus 0.560%, Strontium 0.058%, Chromium 0.008%, Nickel 0.005%, Copper 0.003%, and Manganese 0.003%. The oxide composition includes Aluminum Oxide 1.453%, Magnesium Oxide below the limit of detection, and Potassium Oxide 0.307%.

TABLE III.III. SUMMARIZED XRF RESULTS FOR THE SAMPLE OYSTER

Element		Conc. [% wt.]	Stddev [% wt.]
Calcium	Ca	37.693	0.087
Aluminum Oxide	Al ₂ O ₃	1.784	0.257
Chlorine	Cl	1.160	0.029
Sulfur	S	0.408	0.021
Potassium Oxide	K ₂ O	0.088	0.006
Iron	Fe	0.081	0.008
Strontium	Sr	0.074	0.002
Manganese	Mn	0.012	0.003
Chromium	Cr	0.008	0.004
Nickel	Ni	0.005	0.001
Copper	Cu	0.003	0.001
Zinc	Zn	0.003	0.001

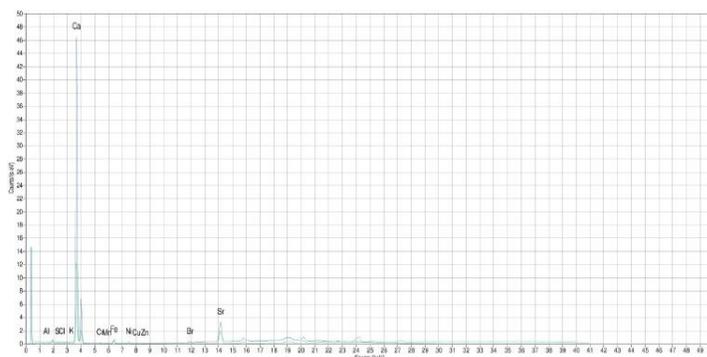


Fig. 3.2. XRF spectra of the sample Oyster

Considering the common elements with higher concentrations that contribute significantly to pollutant adsorption, the concentration percentages in the Oyster shell are: Calcium 37.693% with the standard deviation of 0.087%, Chlorine 1.160%, Sulfur 0.408%, Phosphorus 0.412%, Strontium 0.074%, Chromium 0.008%, Nickel 0.005%, Copper 0.003%, and Manganese 0.012%. The oxide composition in Oyster shells includes Aluminum Oxide 1.784%, Magnesium Oxide 0.966%, and Potassium Oxide 0.088%.

TABLE III.IV. SUMMARIZED XRF RESULTS FOR THE SAMPLE MUSSEL

Element		Conc. [% wt.]	Stddev [% wt.]
Calcium	Ca	38.371	0.088
Aluminum Oxide	Al ₂ O ₃	1.674	0.258
Magnesium Oxide	MgO	1.542	0.998
Chlorine	Cl	0.739	0.026
Sulfur	S	0.155	0.018
Strontium	Sr	0.129	0.002
Potassium Oxide	K ₂ O	0.088	0.007
Chromium	Cr	0.012	0.004
Manganese	Mn	0.005	0.003
Nickel	Ni	0.005	0.001
Copper	Cu	0.003	0.001

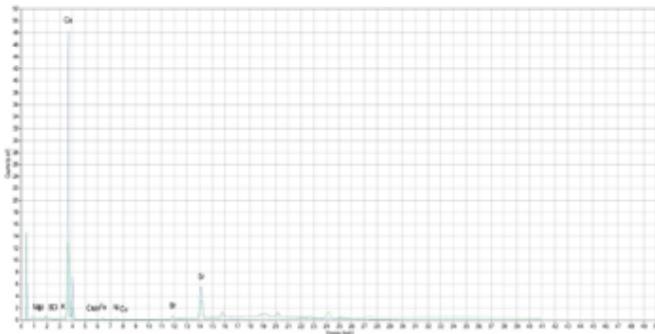


Figure 5.3. XRF spectra of the sample Mussel

In the Mussel shell, the concentration percentages are: Calcium 38.371% with a standard deviation of 0.088%, Chlorine 0.739%, Sulfur 0.155%, Phosphorus 0.424%, Strontium 0.129%, Chromium 0.012%, Nickel 0.005%, Copper 0.003%, and Manganese 0.005%. The oxides in Mussel shells are Aluminum Oxide 1.764%, Magnesium Oxide 1.542%, and Potassium Oxide 0.088%.

With the data shown above, oyster, mussel, and chicken eggshells all contain calcium as the highest concentration element. A higher percentage of calcium in these materials indicates a greater amount of calcium carbonate (CaCO_3), which is used as an air pollutant adsorbent [91].

Chlorine's high reactivity, though having some potential benefits, can greatly worsen air quality by promoting the formation of harmful secondary pollutants. Managing chlorine emissions and exploring alternatives are essential strategies for achieving cleaner air [96]. Sulfur is a common component of acidic pollutants like sulfur dioxide (SO_2). In materials such as oyster shells, egg shells, and mussel shells that contain calcium carbonate (CaCO_3), sulfur can react with calcium to form calcium sulfate (CaSO_4). This chemical reaction helps remove sulfur dioxide from the air by converting it into a less harmful compound [97]. MgO provides several advantages over traditional lime/limestone systems for SO_2 removal, including higher reactivity, reduced scaling and fouling, lower slurry viscosity, and potential environmental benefits. These factors contribute to improved efficiency, lower maintenance costs, and overall better performance in Flue-Gas Desulfurization systems [98]. Aluminum oxide, potassium oxide, and other elements detected in trace amounts are unlikely to significantly influence the adsorption of common air pollutants.

3.2. Thermal Stability of the Shells

TGA analysis used to measure the change in weight of various shell materials as a function of temperature and hence reveal the decomposition patterns of the shells at the temperature range of 30 deg C to 800 deg C [99]. Thermal stability analysis was performed using Perkin Elmer TGA 4000. The graphs obtained from the Thermogravimetric Analysis are presented in Figure 5.4 to 5.6. As shown in the figures, the variation seen in the thermal curve of the oyster, mussel, and chicken eggshell is due to the different structural compositions of the individual shells which has confirmed by the XRF analysis together with CaCO_3 .

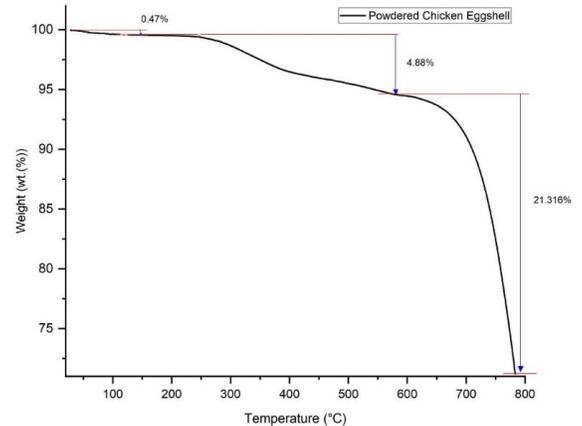


Fig. 3.4. TGA graph of the sample Chicken Eggshell

Figure 3.4 depicts the TGA curve for powdered chicken eggshells, showcasing four stages of thermal decomposition behavior. The initial significant weight loss, occurring between 28.82 deg C and 200.89 deg C and amounting to 0.47%, is primarily attributed to the evaporation of the sample's moisture content. Beyond this, a second notable decline at 574.49 deg C, resulting in a weight loss of 4.88%, is linked to the decomposition of organic materials within the sample. This observation is supported by a comprehensive study examining the thermal decomposition of proteins and lipids within the ranges of 209–309 deg C and 200–635 deg C, respectively [101]. Additionally, research indicates that the stability of calcium carbonate (CaCO_3) from chicken eggshells persists within the temperature range of 250 deg C to 600 deg C [102, 103]. As the temperature escalates further to 782.97 deg C, a drastic 23.32 wt% drop is observed, primarily attributed to the liberation of carbon dioxide from CaCO_3 , consequently leaving behind CaO from the powdered chicken eggshells [104, 105].

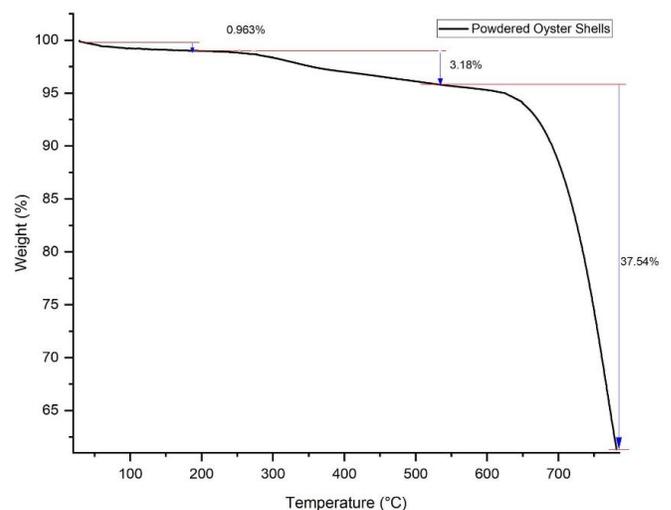


Fig. 3.5. TGA graph of the sample Oyster shell

The oyster shell decomposition pattern is shown in Figure C. Unlike the mussel and eggshell, the oyster shell decomposes in three distinct steps. The first degradation,

which occurs with a weight loss of 0.963%, is due to water evaporation from powdered oyster shells at temperatures ranging from 28.81°C to 192.54°C [113, 114]. As the temperature increases up to 531.64 deg C, a notable decrease in weight (3.18%) is observed due to the deterioration of volatile materials in the sample [115]. Further heating from 531.64 deg C to 782 deg C results in a significant weight loss of 37.54%, attributed to the release of CO₂ from CaCO₃ [110, 116]. This indicates that the crystalline structure of the oyster shell is composed almost exclusively of CaCO₃, with no organic constituents found in either chicken eggshells or mussel shells [117].

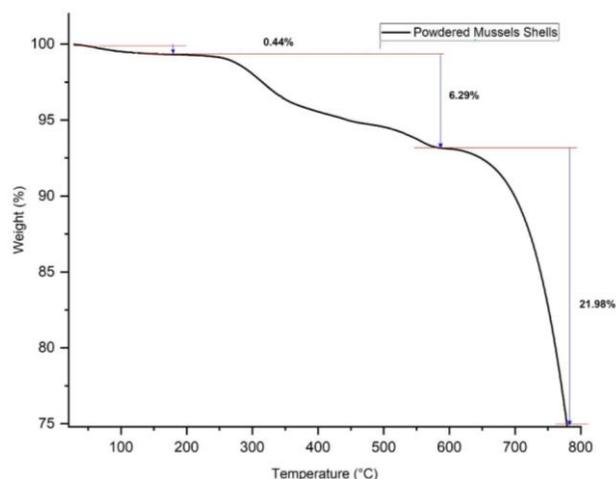


Fig. 3.6. TGA graph of the sample Mussel shell

Figure 3.6 illustrates the thermal decomposition behavior of powdered mussel shells, showcasing four stages of degradation. The initial weight loss of approximately 0.4% occurs between 28.77 deg C and 225.92 deg C, attributed to the loss of water molecules from the crushed mussel shells [106]. A study observed that mussel shell samples undergoing TGA testing at ambient temperatures up to 200 deg C exhibited around 0.4% weight loss due to the release of physically absorbed water. Increasing the temperature up to 666.01 deg C resulted in an additional 6.294% weight loss, likely due to the oxidation and degradation of volatile materials [107]. A drastic weight loss of 21.98% was observed beyond 650 deg C, attributed to the decomposition of the mussel shells [107, 108]. This observation is supported by the study of K.H. Mo et al. (2018), which reported that temperatures between 600-850 deg C caused a more than 40 wt% weight loss due to mussel shell decomposition [109, 110]. Similarly, Chiou et al. observed that oyster shells were almost completely decomposed at temperatures over 760 deg C [110], while Mohamed et al. found a significant reduction in the weight of cockle shells when the temperature was increased from 700 deg C to 900 deg C, due to carbonate decomposition [111]. Safi et al. reported a similar pattern of weight loss with increasing temperature for seashells and typical limestone [112].

The major component of the four types of shells is calcium carbonate (CaCO₃), which decomposes into calcium oxide (CaO) and carbon dioxide (CO₂). The weight loss of

about 37.54% in the shell sample is attributed to the release of CO₂, which constitutes approximately 44% of the weight of CaCO₃ during decomposition. The temperature at which each shell sample reaches the minimum thermal decomposition to CaO varies. For mussel and eggshells, an initial conversion to CaO begins at temperatures of 570 deg C and above. In contrast, oyster shells begin their initial conversion to CaO at a lower temperature of around 531 deg C. This difference is due to the distinct structural compositions of the shells and the varying levels of organic impurities present in some of the samples [117].

3.3 Identification of Compounds

Functional group analysis was performed using Perkin Elmer FT-IR Spectrometer Frontier with FT-IR parameters listed in Table III.V. Baseline correction was applied to the spectrum to improve its quality without distorting the band intensities in the final spectrum.

TABLE III.V PARAMETERS USED FOR FTIR ANALYSIS

Parameters	Parameter Type/Value
Testing Equipment	Perkin Elmer FT-IR Spectrometer Frontier
Technique	Attenuated Total Reflectance (ATR)
Range	4000 – 600 cm ⁻¹
No. of scans	20

The infrared vibration spectra of the samples (Chicken Eggshell, Oyster, and Mussel) were identified to be the following as shown in Table III.VI. The compounds were determined by identifying the characteristic frequencies as absorption/transmittance bands in the infrared spectra of the samples and compared with the characteristic group frequencies of the reference compounds. The peak assignments are summarized in Table III.VII while the FT-IR spectra are shown in Figures 3.7 to 3.9, respectively.

TABLE III.VI. NAME OF THE SAMPLE/S AND THE CORRESPONDING COMPOUND/S IDENTIFIED

Name of Sample/s	Compound/s Present
Crushed Oyster	Calcium Carbonate
Mussel	Calcium Carbonate and Hydroxyl-containing compounds
Chicken Eggshell	Calcium Carbonate

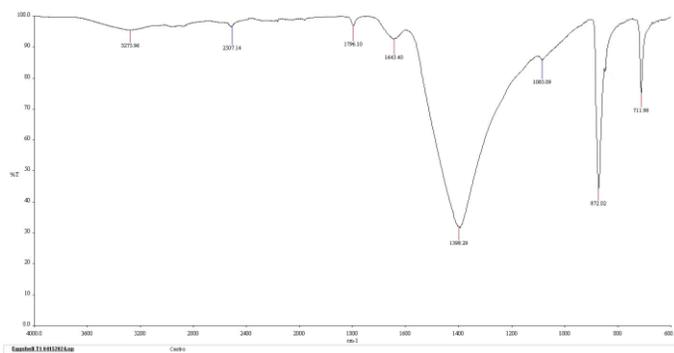


Fig. 3.7. FT-IR spectrum of the Crushed Chicken Eggshell sample

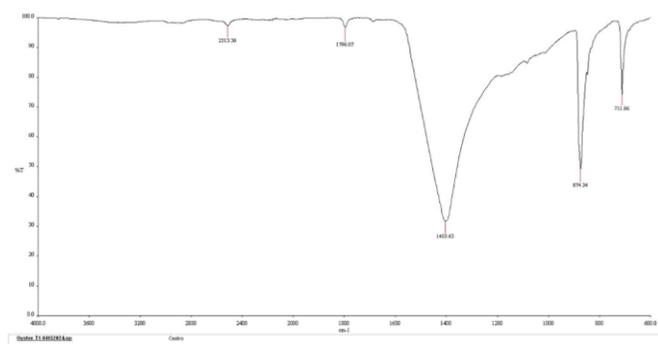


Fig. 3.8. FT-IR spectrum of the Crushed Oyster sample

TABLE III.VII PEAK ASSIGNMENTS IN THE INFRARED SPECTRA OF THE SAMPLES

Calcium Carbonate, Standard *	Frequencies (cm ⁻¹)			Structure/Compound Type*	Bonds*
	Crushed Oyster	Mussel	Chicken Eggshell		
2530	2513.36	3298.13	3275.96	Hydroxyl	O-H Stretch
1805	1796.07	1786.33	1796.10	Carbonate	O-C=O Skeletal vibration (major)
1430	1403.63	1648.66	1643.40	Hydroxyl	O-H Bend
1090		1450.19	1398.29	Carbonate	O-C=O Skeletal vibration (major)
875	874.34	1082.67	1085.09	Carbonate	O-C=O Skeletal vibration (major)
720	711.86	857.17	872.02	Carbonate	O-C=O Skeletal Vibration (minor)
		712.20	711.98	Carbonate	O-C=O Skeletal Vibration (minor)
		699.76		Hydroxyl	O-H Bend

(* References: [1] Spectrum Search Plus Library, Perkin Elmer. [2] Pretsch, E., et al. (2009), Structure Determination of Organic Compounds, 4th Ed., Springer – Verlag Berlin Heidelberg.)

The FTIR spectra can be divided into three broad regions. The first region, from 4000 cm⁻¹ to 3000 cm⁻¹, represents hydrogen bonding. The second region, from 3000 cm⁻¹ to 1500 cm⁻¹, shows functional groups. Meanwhile, the third region reveals the existence of biominerals [118]. Figure 5.7

shows the IR spectrum of the chicken eggshell. The fundamental absorption bands at 712 cm⁻¹, 872 cm⁻¹, and 1399 cm⁻¹ are indications of the asymmetric stretch, out-of-plane bend, and in-plane vibration of C-O bonds of CaCO₃, respectively [119]. The small peak at 3276 cm⁻¹ is attributed to OH group stretching in Ca(OH)₂, which forms upon the exposure of the shell to atmospheric moisture [120]. Similar spectral signals were observed for the mussel shell with absorption bands at 712 cm⁻¹, 858 cm⁻¹, and 1451 cm⁻¹, attributed to the asymmetric stretching, out-of-plane bending, and in-plane vibration of the O-C-O bond of CaCO₃ (7). The oyster shell has characteristic CO₃²⁻ absorption bands at 712 cm⁻¹, 875 cm⁻¹, and 1404 cm⁻¹ [120].

Based on a study determining compounds in IR spectra, the average calcium carbonate standard is typically found at 1430 cm⁻¹. The figures indicate that the most significant peak intensities are as follows: for the chicken eggshell at 1398.29 cm⁻¹, for the mussel shell at 1450.19 cm⁻¹, and for the oyster shell at 1403.63 cm⁻¹. These peaks signify the presence of calcium carbonate as they are close to the calcium carbonate standard [121]. Additionally, the observation by [120] noted that the band at 1430 cm⁻¹ is attributed to the stretching vibration of CaCO₃. This finding is also confirmed by the Perkin Elmer Spectrum Search Plus Library. Comparing the three samples, it can be concluded that oyster and mussel shells have a higher trace of calcium carbonate due to their peaks being closer to the standard value.

Additionally, a sharp peak is also visible between 711–875 cm⁻¹. According to [119], the observable peaks in this range can be associated with the presence of CaCO₃. These peaks are attributed to the in-plane deformation and out-of-plane deformation modes of calcium carbonate, as described by Busca and Resini [123].

Moreover, the rounded peak in the region around 3400-3200 cm⁻¹ which can be seen at the mussel (3299 cm⁻¹) and chicken eggshell (3276 cm⁻¹) is where hydroxyl groups (O-H) appear. Hydroxyl groups are active centers in many catalytic reactions and can play an important role during catalyst preparation [119].

The FTIR analysis of the samples revealed the presence of two distinct compounds pertinent to the testing. Calcium Carbonate was prominently detected and identified in all three samples, namely the oyster, chicken eggshell, and mussel. However, Hydroxyl-containing compounds were exclusively observed in the Mussel sample, indicating a unique chemical composition compared to the other samples.

IV. SUMMARY, CONCLUSION, AND RECCOMENDATION

The primary aim of this research is to analyze and characterize oyster, mussel, and chicken egg shells to assess their suitability for emission pollutant capture in engines. To address the objectives of the study, X-ray Fluorescence Analysis, Thermogravimetric Analysis, and Fourier Transform Infrared Spectroscopy were utilized to characterize the shells. The findings below align with the study's first, second, and third objectives.

4.1. Elemental composition of the shells

X-ray fluorescence spectroscopy (XRF) analyzed oyster, mussel, and chicken eggshells to evaluate their potential as calcium carbonate sources. Calcium carbonate (CaCO_3) is effective in adsorbing air pollutants like sulfur dioxide (SO_2) and nitrogen oxides (NO_x), reducing emissions and neutralizing acidic pollutants. Eggshells are 94% calcium carbonate, while oyster and mussel shells are around 96% and 94% calcium carbonate, respectively. The primary element in all shells is calcium, indicating a high calcium carbonate content. Oyster shells contain 37.693% calcium, while mussel and chicken eggshells contain 38.371% and 35.253%, respectively. Other elements like chlorine, sulfur, and phosphorus contribute to pollutant adsorption. High chlorine reactivity can worsen air quality, but sulfur reacts with calcium carbonate to form less harmful compounds. Magnesium oxide (MgO) in shells improves efficiency in flue-gas desulfurization systems, enhancing pollutant removal. Trace elements like aluminum oxide and potassium oxide have minimal influence on pollutant adsorption.

4.2. Identified Compounds with Potential Affinity for Emission Pollutants

The FTIR analysis categorizes into three regions: hydrogen bonding (4000 cm^{-1} to 3000 cm^{-1}), functional groups (3000 cm^{-1} to 1500 cm^{-1}), and biominerals. Notably, in the chicken eggshell, absorption bands at 712 cm^{-1} , 872 cm^{-1} , and 1399 cm^{-1} correspond to C-O bonds of CaCO_3 , with a minor peak at 3276 cm^{-1} indicating $\text{Ca}(\text{OH})_2$. Similar signals in the mussel and oyster shells confirm the presence of CaCO_3 . The characteristic absorption bands at 712 cm^{-1} , 875 cm^{-1} , and 1404 cm^{-1} suggest the presence of CO_3^{2-} ions. Peak intensities for calcium carbonate, found near 1430 cm^{-1} , are highest in the chicken eggshell (1398.29 cm^{-1}), followed by the mussel shell (1450.19 cm^{-1}) and oyster shell (1403.63 cm^{-1}). Additionally, a sharp peak at $711\text{--}875\text{ cm}^{-1}$ confirms the presence of CaCO_3 . Hydroxyl groups are evident in the mussel and chicken eggshell, suggesting their catalytic role. Overall, all samples contain calcium carbonate, while only the mussel shell exhibits hydroxyl-containing compounds.

4.3. Thermal Stability of the Shells under Simulated Temperatures

Thermogravimetric Analysis (TGA) was conducted to analyze the weight change of chicken eggshell, oyster, and mussel as temperature varied from $30\text{ }^\circ\text{C}$ to $800\text{ }^\circ\text{C}$ using Perkin Elmer TGA 4000. The thermal curves differed due to varying structural compositions, confirmed by X-ray Fluorescence Analysis. Chicken eggshell decomposed in four stages, starting with 0.47% weight loss due to water evaporation. At 574.49°C , a 4.88% weight loss occurred due to organic impurities like protein, while calcium carbonate (CaCO_3) remained stable between 250°C and 600°C . A significant drop of 23.32wt% at 782.97°C indicated CO_2 release from CaCO_3 decomposition. Oyster shell decomposed in three steps, with a 0.963% weight loss from water evaporation. At 531.64°C , a 3.18% weight loss was observed

due to volatile material degradation, followed by a 37.54wt% loss at 782°C from CaCO_3 decomposition. Mussel shell decomposed in four stages, with a 0.4% initial weight loss from water evaporation and a significant 21.98% loss at temperatures beyond 600°C due to CaCO_3 decomposition. The differences in decomposition temperatures are attributed to varying structural compositions and organic impurities.

V. CONCLUSION

In this study, oyster shells, mussel shells, and chicken eggshells were comprehensively characterized and evaluated for their potential as sustainable sorbents for emission pollutant capture in exhaust systems. The investigation encompassed X-ray Fluorescence Analysis (XRF), Fourier Transformed Infrared Spectroscopy (FTIR), Thermo-Gravimetric Analysis (TGA), and identification of compounds to determine their elemental composition, thermal stability, and adsorption capabilities.

XRF analysis revealed that all three shell types predominantly consist of calcium carbonate (CaCO_3), with minor impurities. Calcium, the primary constituent, plays a crucial role in pollutant adsorption due to the presence of CaCO_3 . Despite variations in elemental composition, calcium concentrations were relatively consistent among the shells, indicating their suitability for pollutant capture. While the presence of elements like sulfur and chlorine could enhance adsorption capacities or pose challenges, their quantities were within acceptable ranges.

TGA analysis revealed the thermal behavior of the shells under simulated conditions. Oyster shells exhibited a distinct three-step decomposition pattern, suggesting a crystalline structure primarily composed of CaCO_3 . The decomposition of calcium carbonate to calcium oxide initiated within the temperature range of approximately 531°C to 782°C for oyster shells. Conversely, mussel and chicken eggshells displayed a four-step decomposition process, indicating structural disparities and differing levels of organic impurities. For mussel shells, the onset of calcium carbonate decomposition occurred within the temperature range of approximately 225.92°C to 600.01°C . Similarly, for chicken eggshells, decomposition commenced at temperatures ranging from approximately 574.49°C to 782.97°C . The liberation of CO_2 during decomposition unequivocally affirmed the presence of CaCO_3 , an indispensable component for effective pollutant capture.

FTIR analysis confirmed the presence of calcium carbonate in all three shell types. Characteristic absorption bands corresponding to CaCO_3 were observed, validating their potential for pollutant adsorption. Additionally, hydroxyl-containing compounds were exclusively detected in mussel shells, suggesting unique chemical properties that could influence adsorption behavior.

Based on the comprehensive analysis, mussel shells emerge as the most promising sorbent for emission pollutant capture. TGA data reveals their robust thermal stability, with decomposition of calcium carbonate initiating at temperatures above 600°C , ideal for high-temperature applications. XRF analysis indicates mussel shells' elemental composition,

primarily calcium, conducive to pollutant adsorption, while minor impurities like sulfur and chlorine remain within acceptable ranges. FTIR confirms the presence of calcium carbonate and unique hydroxyl-containing compounds in mussel shells, enhancing their adsorption capabilities. Overall, mussel shells offer the optimal combination of thermal stability, elemental composition, and functional groups for effective emission pollutant capture in exhaust systems.

4.5. Recommendations

In accordance with the findings established in this study, the researchers of the study suggest the following:

- Perform X-Ray Diffraction analysis to test the amount of calcium carbonate in the mussel shell, as this will provide precise data on the primary component, ensuring the shell's capacity for sorbent applications.
- Perform Scanning Electron Microscopy analysis to determine the crystalline structure of the mussel shell, crucial for understanding its physical properties and optimizing its pollutant adsorption capacity.
- Further investigate optimal processing methods to enhance the sorption capacity of mussel shells for emission pollutant capture
- Investigate other processes, including the use of catalysts, to easily calcinate the calcium carbonate, breaking it down into calcium oxide and carbon dioxide, thereby enhancing the reactivity and adsorption potential
- Investigate alternative methods for breaking down calcium carbonate into calcium oxide and carbon dioxide, to identify more efficient or cost-effective approaches
- Develop and field-test sorbent-based instruments incorporating mussel shells for real-world pollutant capture, to evaluate their practical application and effectiveness in actual condition
- Evaluate the effect of particle size and surface morphology on the adsorption efficiency of mussel shell sorbents, as these factors significantly influence the sorbent's capacity to capture pollutants.
- Research the effectiveness of mussel shell sorbents in capturing a variety of pollutants, including sulfur dioxide (SO₂) and nitrogen oxides (NO_x), to ensure their broad applicability and effectiveness.

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