Nigerian Research Journal of Chemical Sciences, Vol. 6, 2019

CHARACTERIZATION OF ADSORBENTS FROM ANIMAL SOURCE (*SHELLS OF CLAM AND OYSTER*) USING INFRARED SPECTROMETRIC TECHNIQUE

*Chikwe, T.N., Ogbole, S.N.
Department of Pure and Industrial Chemistry,
University of Port Harcourt,
P.M.B 5323, Choba, Port Harcourt, Nigeria.
*Corresponding author: templechikwe@yahoo.co.uk; temple.chikwe@uniport.edu.ng

ABSTRACT

Shells of aquatic organisms, Clams (Thales) and Oysters, were analyzed in their powdery form by Infrared Spectrometric technique using Nicolet IS5 Fourier Transform Spectrometer to identify the functional groups in the shells. Results obtained showed that the predominant functional group in both shells is carbonate ion (CO_3^{2-}). This was indicated by the peaks at wavelength ranges of 1380 – 1370cm^{-1} and 1157 – 1154cm^{-1} representing symmetric and asymmetric stretching vibrations respectively as well as 862 – 860cm^{-1} and 771 – 722cm^{-1} representing out of plane and in plane bending vibrations respectively. Carbonate ion is a highly polarized group owing to its electronegativity and high dipole moment. The shells of Clam and Oyster also contain other highly polarized group such as bicarbonate ion (HCO_3^-), primary amines (NH_2^-) and alkyl halides ($C\text{-}Br^-$) at wavelength ranges of 1100 – 600cm^{-1}, 3500 – 3400cm^{-1} and 690 – 515 cm^{-1} respectively. The impact these functional groups have in the adsorption characteristics of the shells (adsorbent) depends on their influence on the shell's molecular polarizability as well as the adsorbate – adsorbent interactions. The higher the molecular polarizability of the powdery shells which is a function of the number of polar groups in these shells, the better the adsorption capacity of the adsorbents. The shells of Oyster showed a better adsorption characteristic due to the presence of the carbonyl group at a wavelength range of 1790 – 1800 cm^{-1}which indicates either the presence of aldehydes, ketones, carboxylic acids or their derivatives. Carboxylic acids are the most polarized organic functional group due to their ability to form hydrogen bond, presence of two electronegative atoms (oxygen) as well as a high dipole moment.

Key Words: Adsorbate, clams shell, electronegativity, oyster shell, polarizability, wavelength.

INTRODUCTION

The need to characterize the surfaces of porous and finely distributed materials began during the 19th century which coincided with the period of industrialization. Currently, all the methods used for adsorption surface measurements are standardized in industrial countries of the world [1]. Adsorption is the clinging of molecules, ions or atoms from matter to a surface. Adsorption is a surface phenomenon different from absorption which involves the entire material volume. The process of adsorption creates a film of the adsorbate (liquid material) on the surface of the adsorbent (solid) [2]. Adsorbents are insoluble materials with tiny or capillary holes which bind liquid or gaseous molecules to their surface. A material is said to be an adsorbent if it has the ability to contain a specific amount of liquid in small chambers similar to a sponge [3]. Considering the fact that sponges are members of the phylum *porifera* within the *Animalia* kingdom, it becomes imperative to try the adsorption capacities of several other animal sources, for instance, shells of aquatic organisms, like Clams and Oyster, could serve as adsorbents when prepared in a powdery form. Clams is a common name for different types of bivalve mollusca. They are sometimes called Thales, and they fall within the Animalia kingdom. Clams have two shells of equal sizes connected by two adductor muscles and they have a strong burrowing foot. There are different classes of Clams ranging from hard shell Clams, soft shell Clams to manila Clams [4-5]. Oysters, just like Clams, are within the family of bivalve Mollusca within the Animalia kingdom. Some classes of Oysters are also referred to as Clams. However, in the culinary sense, Clams do not live attached to a substrate but Oysters do [6]. Some pictures of Clams and Oysters are shown in Figures 1 & 2.

Fig. 1: Hard Shell Clams or Thales

Fig. 2: Oyster Shells

Some of the important applications of adsorption include; treatment of oil spillage using agricultural waste, removal of moisture using silica gel, softening of water using ion exchange method, removal of colored impurities from sugar using charcoal powder, etc [7].

Infrared (IR) spectroscopy is the relationship between infrared radiation and matter. Infrared radiation is an electromagnetic radiation that has wavelengths longer than those of visible lights [8]. The infrared portion of the electromagnetic spectrum is divided based on their relationship to the visible spectrum. The three regions of an infrared spectrum are near, mid and far- infrared. The fundamental vibrations which give essential information about the sample composition in terms of purity and chemical groups present are studied using the mid infrared spectroscopy and this corresponds to 4000 – 400 cm^{-1}[9]. The basic function of infrared spectroscopy is in functional group identification. It therefore does not have the ability to determine the whole structure of a molecule, neither does it give the percentage composition of each of the components in the molecule [8]. The influence of functional groups on adsorption is dependent on the relationship of its influence on molecular polarizability and adsorbate-adsorbent interactions. Generally, increase in polarizability is directly proportional to increase in the volume occupied by electrons because larger atoms have more loosely bound electrons compared to smaller atoms. Larger molecules are generally more polarizable than smaller ones. Water for instance is a polar molecule but alkanes and other hydrophobic molecules are more polarizable [10-11]. The aim of this study is to characterize the shells of aquatic animals such as Clams and Oyster using infrared spectroscopy in other to find out the functional groups in these shells and their impact on adsorption, and hence to confirm their suitability as a bio remediating agent.

Shells of Clams and Oyster are nonedible sources obtained from these aquatic organisms (Clams and Oyster) which if found suitable could provide cheaper and more environmentally friendly method of treating oil spillage as well as proper use in other adsorption applications.

MATERIALS AND METHODS

Sample Collection and Preparation.

Clams and Oyster shells were purchased from local fishermen at Borokiri market in Rivers State, Nigeria. These shells were properly washed using distilled water and oven dried at 35°C at a well monitored and controlled laboratory temperature for 72 hours. The dried shells were thereafter crushed using electrical grinder machine, subjected to shaking using magnetic shaker into fine particles of 60 µm and then characterized using infrared spectroscopic technique.

FT –IR Characterization

Powdery particles of the shells of Clams (PCS) and shells of Oyster (POS) were successively subjected to Fourier transform infrared (FT –IR) characterization by the solid state method. They were characterized using ASTM D2621 [12]. Potassium bromide (KBr) equivalent to 100 mg was properly mixed with one milligram of PCS and POS respectively using small plastic pestle and mortal. The KBr – oyster shell’s powder mixture was added to sample compartment and gently squeezed for transparent disc formation. The Oyster shell – KBr disc was thereafter placed in the equipment and carefully analyzed. The same procedure was adopted for powdery samples of Clams shell. A beam of infrared light was passed through an interferometer (Shimadzu IRAffinity-1 FTIR spectrophotometer, Japan) which splits into two separate beams. Each of the beams passes through the sample and reference respectively. The distribution of the infrared light that passes through the interferometer was altered using a moving mirror placed inside the apparatus. The signal directly recorded, called an "interferogram", represents light output as a function of mirror position. The beams pass through a splitter and then reflected back towards a detector. The splitter alternates the beams that enter the detector. A data-processing technique called Fourier transform turns this raw data into the desired result which is the sample's spectrum [12].

RESULTSAND DISCUSSION

Table1: Functional Groups Obtained From IR Spectrum of Powdered Clams or Thales Shells (PCS)

Peak	Wavelength (cm^1)	Mode of Vibration	Functional Group
P1	3500-3400	In plane N-H bending	primary amine
P2	3000 - 2840	C-H symmetric stretching	alkane
P3	1380-1370	CO_3^{2-}asymmetric stretching	carbonate ion
P4	1157-1154	CO_3^{2-}symmetric stretching	carbonate ion
P5	1100-600	HCO_3^- symmetric stretching	bicarbonate ion
P6	862 - 860	Out of plane vibrational bending of CO_3^{2-}	carbonate ion
P7	771- 722	In plane vibrational bending of CO_3^{2-}	carbonate ion
P8	690- 515	C-Br$^-$stretching	halo compound

The major functional groups obtained from IR spectrum of PCS were listed in Table 1. The prominent functional groups indicated from IR spectrum as shown in figure 3 include a medium in plane N-H bending vibration of primary amines at a wavelength of 3500 – 3400 cm-1 and a medium C-H stretching of alkanes at a wavelength of 3000 – 2840 cm^{-1}. Asymmetric and symmetric stretching of carbonate ions at wavelength ranges of 1380 – 1370 and 1157 – 1154 cm-1 respectively confirms the presence of carbonate ions. Out of plane vibrational bending and in plane vibrational bending of carbonate ions at wavelength ranges of 862 -860 and 771 – 722 cm^{-1} respectively confirm carbonate ions as the most predominant functional group in PCS. The presence of the halogen functional group is indicated by C-Br stretching at a wavelength of 690 - 515 cm^{-1}.

Table 2: Functional Groups Obtained From IR Spectrum of Powdered Oyster Shells

Peak	Wavelength (cm^1)	Mode of Vibration	Functional Group
P1	3500-3400	In plane N-H bending	primary amine
P2	3000 - 2840	C-H symmetric stretching	alkane
P3	1790 - 1800	C=O stretching	carbonyl
P4	1370-1380	CO_3^{2-}asymmetric stretching	carbonate ion
P5	1157-1154	CO_3^{2-}symmetric stretching	carbonate ion
P6	1100-600	HCO_3^- symmetric stretching	bicarbonate ion
P7	862 - 860	Out of plane vibrational bending of CO_3^{2-}	carbonate ion
P8	771- 722	In plane vibrational bending of CO_3^{2-}	carbonate ion
P9	690- 515	C-Br$^-$ stretching	halo compound

All the functional groups in PCS are also present in POS as shown in Table 2 and can be seen from figures 3 and 4, However the IR spectrum of POS also contains C=O stretching of carbonyl groups at the wavelength range of 1790 -1800 cm^{-1}.

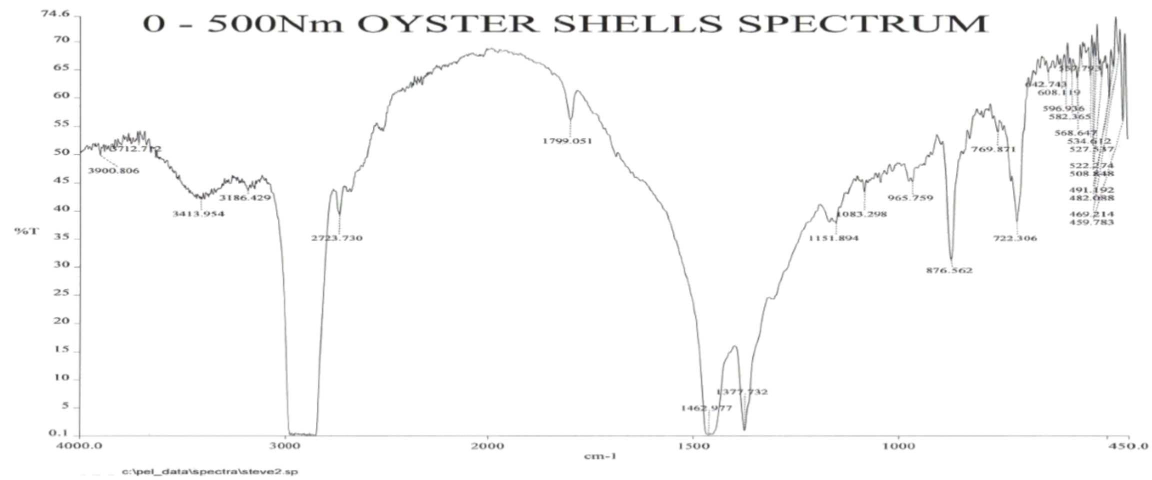

Fig. 3: Infrared Spectrum of Powdered Clams or Thales Shells (PCS).

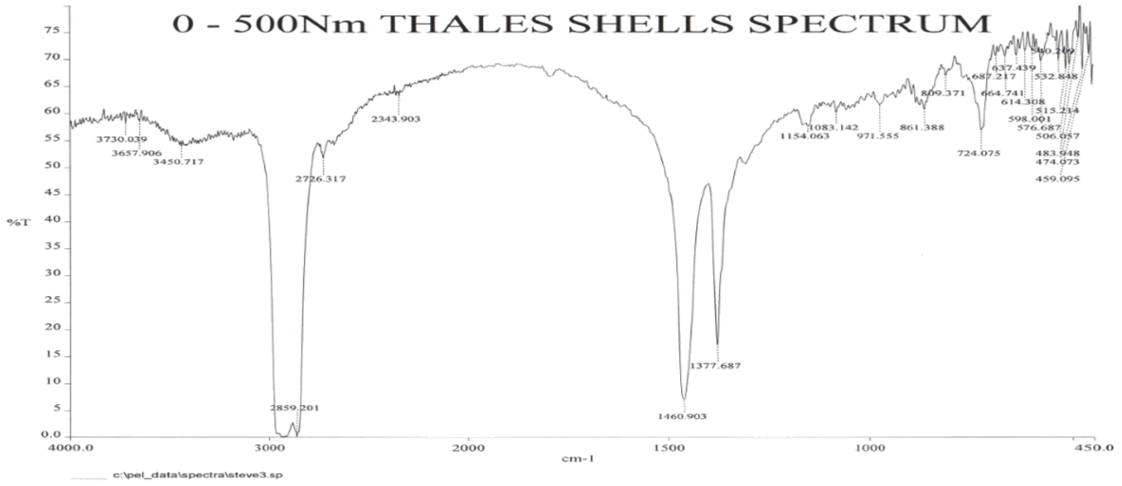

Fig. 4: Infrared Spectrum of Powdered Oyster Shells (POS).

Figures 3 and 4 show the infrared spectrum of powdery clam and oyster shells respectively

Infrared spectroscopy gives an x-ray into the internal structure of a substance thereby revealing the elements and functional groups present in the substance, this is very key in appreciating why certain substances display specific properties as well as the probability of their suitability in specific applications [13]. The functional groups are basically identified by the shape of the peak made possible from stretching and bending vibrations, peak intensity made evident from the height and size of the peak as well as the wavelength at which the peaks elute [14]. The presence of polar groups in PCS and POS as shown in the functional groups explains part of the reason for their adsorption properties. Polarizability is the ability for molecules to separately form positive and negative charges instantaneously. Polarizability is a property of matter which determines the response of a bound system to external influences thereby providing vital information on the molecules internal structure. The higher the polarizability of a molecule, the higher the tendency of its atoms to release electrons and the higher the adsorption capacity of the molecule [10]. Larger atoms have proven to be more polar than smaller atoms because of the ease with which they release electrons. A molecules polarity is primarily dependent on the ease at which it can form hydrogen bond, the number of electronegative atoms, the size of the atoms (the polarizability of the bonds / atoms) and the net dipole moment of the molecule. Based on the aforementioned rules, it can be deduced that alkanes are the least polar group amongst the organic functional groups. The alkanes have no hydrogen bonding, no electronegative atoms and a very small net dipole moment [15]. The dipole moment of a molecule is a vector quantity whose direction is assigned from its partial positive to partial negative charge [16]. Though PCS and POS contains alkane functional groups with low polarity as shown in Tables 1 and 2, it is important to note that these shells (PCS and POS) also contains functional groups with very high polarity thereby making them very good adsorbents.

Tables 1 and 2 shows that both shells contains amines, these amines are in the form of biogenic amines. The presence of amines in the shells of aquatic organisms such as Clams and Oyster is a consequence of different factors such as the presence of free amino acids, microorganism producers of decarboxylase enzymes and variations in food processing and storage. Amines have the ability to undergo hydrogen bonding which is the most important prerequisite for polarizability [17].

Results from the IR spectra of figures 3 and 4 as well as Tables 1 and 2 show the presence of carbonate ions in both shells (PCS and POS). IR spectra of both shells show that carbonate ion is the most predominant ion in both shells (PCS and POS). This is confirmed from the stretching and bending vibrations as well as in and out of plane bending vibrations at different wavelengths within the mid infrared spectroscopy. The presence of carbonate ions in both shells is also a confirmation that calcite and aragonite are key components of Mollusca species [10]. The intercalated organic matrix of these shells and their characteristics are important in the shell's crystal orientation, nucleation and size regulation. It also contributes to the biomechanical properties of both shells (PCS and POS).The carbonate ion plays a central role in the biochemical formation of the shells of aquatic life, which is an important path for carbon dioxide sequestration. As a divalent anion with three electronegative atoms (oxygen), carbonate has a strong polarizing effect on surrounding water molecules. It therefore becomes difficult to effectively describe accurately aquatic systems without including polarization [18]. Results also show the presence of bicarbonate ions and alkyl halides (halo compounds) in both shells (PCS and POS). Bicarbonate ions just like carbonate ions are highly polarizable because of their electronegativity, however they may be more polarizable than the alkyl halides. Alkyl halides are also very polarizable because of the presence of a polar atom (Bromine) [11]. Table 2 shows the presence of carbonyl group in the shells of Oyster which is not present in the shells of Clam as confirmed in Table 1. The carbonyl groups are found in functional groups such as carboxylic acid, aldehydes, ketones, acid anhydrides etc and these functional groups are highly polarizable. The presence of carbonyl group increases the probability of having any of these highly polarizable functional groups in the shells of Oyster (POS) thereby making it a better adsorbent compared to the shells of Clams (PCS). Carboxylic acids are the most polarizable organic functional group because they can undergo hydrogen bonding extensively. They have a dipole moment as well as two electronegative atoms [15].

Polarizability also influences the adsorbate (liquid) / adsorbent (solid) relationship which is a function of the bonding requirements (ionic, covalent or metallic) of the atoms on the surface of the adsorbents [1]. Adsorption is a consequence of surface energy just like surface tension. However atoms on the surface of the adsorbents (PCS and POS) are not totally surrounded by other adsorbent atoms. PCS and POS attract adsorbates through a process of phyisisorption. As such the electronic structure of the atoms or molecule of the adsorbents is not changed upon adsorption [2].

CONCLUSION

Clams and oysters are aquatic organisms within the animal kingdom classified as bivalve Mollusca basically because of the nature of their shells. Identification of the functional groups in the shells of clams and oyster using Infrared spectroscopic technique is very important in knowing the internal structure of these shells as well as their adsorption characteristics. Both shells contains highly polarizable groups such as amines, bicarbonates, carbonates and halo compounds (alkyl halides) hence are very good adsorbents. Carbonates are the most predominant group in these shells which is not unconnected with the fact that bicarbonates play very important role in the biochemical formations of the shells of aquatic lives. The shells of oysters showed better adsorption characteristic due to the presence of a carbonyl group. The influence of functional groups on adsorption is dependent on the relationship of its influence on molecular polarizability and adsorbate-adsorbent interactions hence, the more the number of polarizable groups within the internal structure of an adsorbent the better the adsorption characteristics of the adsorbent as well as is adsorbate - adsorbent relationship.

REFERENCES

1. Roben, E. (1994). Some intriguing items in the history of adsorption. Studies in *Surface Science and Catalysis*, 87, 109 – 118
2. Jayaweera, S.A.A. & Robens, E. (2014). Early History of Adsorption Measurements. *Adsorption Science and Technology*, 1, 67.
3. Rouquerol, F., Llewellyn, P., Maurin, G. & Sing, K. (2013). Adsorption by Powders and Porous Solids. *Academic Press 2nd Edition, 646*
4. Elliot, D. (2013). "Ming the Clam, World's Oldest Animal, Was Actually 507 Years Old. *Bangor University, Wales, United Kingdom, 2nd Edition.*
5. Clam Encyclopædia Britannica (2016).
6. Newell, R.I.E., Fisher, T.R., Holyoke, R.R. & Cornwell, J.C. (2005). Influence of eastern oysters on nitrogen and phosphorus regeneration in Chesapeake Bay, USA. *Vol. 47 (NATO Science Series IV: Earth and Environmental Sciences ed.). Netherlands: Springer, 93–120.*
7. Cheraghian, G. (2017). Evaluation of Clay and Fumed Silica Nanoparticles on Adsorption of Surfactant Polymer during Enhanced Oil Recovery. *Journal of the Japan Petroleum Institute*, 60 (2), 85–94.

8. Demirdöven, N., Cheatum, C.M., Chung, H.S., Khalil, M., Knoester, J. & Tokmakoff, A. (2004). Two-Dimensional Infrared Spectroscopy of Antiparallel Beta-Sheet Secondary Structure. *Journal of the American Chemical Society*, 126 (25), 7981–90.
9. Hargate, G. (2006). A Randomised Double-Blind Study Comparing The Effect Of 1072-nm Light Against Placebo For The Treatment Of Herpes Labialis. *Clinical and Experimental Dermatology,* 31 (5): 638–41
10. Mason, P.E., Wernersson, E., & Jungwirth, P. (2012). Accurate Description of Aqueous Carbonate Ions: An Effective Polarization Model Verified by Neutron Scattering.*Journal of Physical Chemistry*, 116 (28), 8145–8153.
11. Zhou, L., Lee, F.X., Wilcox, W. & Christensen, J. (2002). Magnetic polarizability of hadrons from lattice QCD. *European Organization for Nuclear Research*.
12. American Standard for Testing and Materials, ASTM D2621 (1987). Infrared Identification of Vehicle Solids from Solvent Reducible Paints. Vol 3
13. Kohli, K., Davies, G., Vinh, N., West, D., Estreicher, S., Gregorkiewicz, T., Izeddin, I. & Itoh, K. (2006). Isotope Dependence of the Lifetime of the 1136-cm-1 Vibration of Oxygen in Silicon. *Physical Review Letters,* 96 (22), 225503.
14. Villar, A., Gorritxategi, E., Aranzabe, E., Fernandez, S., Otaduy, D. & Fernandez, L.A. (2012). Low-cost visible–near infrared sensor for on-line monitoring of fat and fatty acids content during the manufacturing process of the milk. *Food Chemistry*, 135 (4), 2756–2760.
15. Munn, R.W. & Popelier P. L. A. (2004). Distributed polarizability analysis for Para-nitro aniline and meta-nitro aniline: Functional group and charge-transfer contributions. *Department of Chemistry, UMIST, Manchester, M60 1QD, United Kingdom.*
16. *Housecroft, C.E. & Alan, G.S. (2008). Inorganic Chemistry. 3rd edition. Harlow: Pearson Education, 44-46*
17. Chenzhong, C., Hua, Y., Shengli, L., & Rongjin, Z. (2000). On Molecular Polarizability: 3. Relationship to the Ionization Potential of Haloalkanes, Amines, Alcohols, and Ethers. *Journal of Chemical Information and Computer Science, 40* (4), 1010–1014
18. Martelli, F., Jeanvoine, Y., Vercouter T., Beuchat, C., Vuilleumier, R. & Spezia, R. (2014). Hydration properties of lanthanoid (III) carbonate complexes in liquid water determined by polarizable molecular dynamics simulations. *Physical Chemistry Chemical Physics, 16, 3693.*