Physicochemical Characterization of Hymenopterasphecidae (mud-wasp) nest

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Abstract

Hymenoptera sphecidae (mud-wasp) nests were harvested and evaluated for their physicochemical properties. Physicochemical characterization of mud-wasp nest gave the following values: pH 6.54; abrasion resistance, 95.10%; bulk density, 1.27 (g/mL); total surface charge, 1.348 (mmol H¹/kg); iodine adsorption number (IAN), 0.1656 (mmol/g); total surface area, 6.335 (g/mg²M): clay, 10.96%; silt, 15.52%; sand, 73.52%. Spectrophotometric analysis of Hymenoptera sphecidaenas was performed using XRF, XRD and FTIR spectroscopy. XRF data revealed the presence of SiO₂, and Al₂O₃ in appreciable quantities, while Fe₂O₃, CaO and MgO were in minor quantities. Na₂O and K₂O were however found to be present in trace amounts. Infrared spectral analysis showed that the sample is a composite of quartz, feldspar, kaolinite and montmorillonite. The dominant presence of quartz was further confirmed by PXRD which also revealed the presence of halloysites.

Keywords: Mud-wasp nest, quartz, feldspar, kaolinite, montmorillonite and halloysite.

Introduction

Hymenoptera sphecidae (mud-wasp) is a species of solitary wasps which construct nests primarily from mud, which they plaster on horizontal and vertical surfaces including walls, plant stems and others¹². These mud-wasp nests when left undisturbed for extended periods, deface the aesthetics of such buildings. When removed, the nest could be utilized gainfully instead of being thrown away as an unwanted material. Over the years, increased industrialization and urbanization has led to the disposal of hazardous substances such as heavy metals into the environment.¹ These industrial activities include processes of textile manufacturing, fertilizer applications, glass and ceramics, mining, electroplating, metal finishing, pulp and paper industries, petroleum and others.⁴⁶. Metallic elements that have a density greater than or equal to 6.0g/cm³ are regarded as heavy metals.⁵. Metals that fall into this category include lead (11.34g/cm³), copper (8.95g/cm³), chromium (7.19g/cm³), cadmium (8.65g/cm³), among others⁵. The discharge of waste containing heavy metal into the environment causes serious soil and water pollution, endangering the quality of natural resources and water used for domestic applications. Heavy metals have bio-accumulating tendency and because they are also toxic in the environment, especially as most of them are carcinogenic, a problem assumed to be related to their electronic structure⁶⁸, there is a need to considerably reduce their levels in industrial and municipal effluents to meet regulatory standards before final discharge into the environment.

Conventional methods used for the removal of heavy metals including floatation, chemical precipitation, solvent extraction, ion exchange, oxidation, reduction, filtration, reverse osmosis and membrane technologies⁹. These have been found to be operational at very high cost and most times are ineffective at low concentrations of the pollutant metals¹⁰. Hence, the search for alternative metal removal techniques which are based on metal-sequestering properties of certain natural materials¹¹.

Though numerous adsorbents including commercial activated carbons have been developed and applied in chemical techniques for heavy metal removal from contaminated waste water, the high cost of these materials coupled with their failure to adsorb a range of metal ions simultaneously has been a major setback¹²; hence further research into the potential application of low-cost adsorbent materials is necessary for heavy metal removal from effluents. The use of innovative, cheap adsorbents including activated carbons generated from agricultural by-products and biosorbents has been extensively reported¹³.

The present study sought to characterize Hymenoptera sphecidae (mud-wasp) nests and ascertain their potential for gainful applications.

Material and Methods

Analytical grade reagents were used without further purification. Mud-wasp nest samples were collected from the walls of buildings in Makurdi metropolis, Benue State, Nigeria using plastic trowels. They were air-dried, ground with a laboratory porcelain mortar and pestle, and sieved through a 2 mm mesh. The samples were then stored in clean dry plastic sample containers and properly labelled.

Physicochemical Characterization: Determination of pH:
1.0g portion of the prepared sample was added to 100mL of distilled water in a 150mL beaker. The mixture was stirred...
Determination of bulk density: The tamping method described by Ahmedna et al.\textsuperscript{13} was employed for the determination of bulk density. In this method, 2.0 g portion of mud-wasp nest was weighed and placed in a dry graduated 5mL measuring cylinder. The cylinder was then tapped until it completely occupied a minimum volume. Bulk density was then calculated using the expression in equation (1).

$$\rho_B (g/mL) = \frac{m}{V_{\min}}$$

(1)

where $m$ = mass of mud-wasp nest, $V_{\min}$ = minimum volume of mud-wasp nest in measuring cylinder.

Determination of Porosity: 1.0 g mud-wasp nest sample was weighed out and dispersed in 50 mL distilled water in a graduated tube. The mixture was centrifuged in a Hermle Labnet Z206A model centrifuge for 10 minutes at 5000 rpm. The resulting volume was read as $V_w$ and recorded and porosity calculated using equation (2).

$$\alpha = \frac{V_w}{V_T}$$

(2)

Where $V_w$ = volume of water taken
$V_T$ = volume resulting after the dispersion of mud-wasp nest.

Determination of moisture content: The moisture content was determined by the procedure given by the Association of Official Analytical Chemists (AOAC)\textsuperscript{14}.

Determination of attrition: Attrition was determined as described by Toles et al.\textsuperscript{15}. In this method, 20g portion of the prepared sample was weighed and dispersed in 100mL sodium acetate-acetic acid buffer of pH 4.0 prepared by mixing aqueous 0.1 M CH$_3$COONa solution and commercial CH$_3$COOH in the ratio 1:5.5 in a 250mL glass beaker and left to stand for 2 h at room temperature. The suspension was filtered through a 2mm sieve and the amount of mud-wasp nest sample retained was quantitatively transferred into a pre-weighed aluminium pan and dried in an oven at 105°C. Attrition was calculated as the ratio of mass loss of the mud-wasp nest to the initial mass expressed as a percentage from the equation(3).

$$\% \text{Attrition} = \frac{m_i - m_f}{m_i} \times 100$$

(3)

Where $m_i$ = initial mass of mud-wasp nest, $m_f$ = final mass of mud-wasp nest.

Determination of iodine adsorption number (IAN): The iodine adsorption number was determined by the procedure described by Okieimen et al.\textsuperscript{16}. In this method, 0.5g portion of mud-wasp nest was slurred with excess aqueous 0.05M iodine solution in a 250mL glass beaker. The content was then swirled vigorously for 10 minutes and the mixture filtered through a funnel impregnated with glass wool. A portion of the filtrate was back-titrated with a standard solution of thiosulphate. The mass (mg) of iodide consumed per gram of mud-wasp nest constitute the iodine number.

Determination of surface area of nest material: Surface area (S.A.) was calculated as the inverse of the iodine number\textsuperscript{16}.

$$S. \text{A.} = \frac{1}{\text{IAN}}$$

(4)

Determination of titrable surface charge: The Boehm titration described by Van-Winkle\textsuperscript{17} was employed in the determination of titrable surface functional groups. 1.0g portion of mud-wasp nest was suspended in 50mL aqueous 0.1 M NaOH solution with occasional stirring for 12 h. The slurry was then filtered through glass wool impregnated in the stem of a plastic funnel. 10mL aliquots of the filtrate were added to 15mL of standard aqueous 0.1M HCl solution and the resulting solution was back-titrated with standard aqueous 0.1M NaOH solution. The volume of NaOH required to neutralize the sample was converted into titrable negative surface charge by expressing the result as millimoles H$^+$ ions consumed by excess OH$^-$ ions per gram of sample.

Determination of particle size distribution: Particle size distribution was determined by the hydrometer method\textsuperscript{18}. 50 g of 2 mm sieved mud-wasp nest sample was weighed into a 250 mL glass beaker. 100 mL aqueous sodium hexameta phosphate (calgon) solution was added into the beaker followed by 100 mL of distilled water. The suspension obtained was stirred with a glass rod and left to stand for 30 minutes with occasional stirring. The suspension was transferred completely into a 100 mL measuring cylinder and made up to the mark with distilled water. Before taking hydrometer readings, the suspension was thoroughly mixed with a glass rod making sure that the sediments at the bottom of the cylinder were thoroughly disturbed. A soil hydrometer was then lowered gently into the suspension and readings taken after 40 seconds. The suspension was then allowed to stand for 2 h and hydrometer readings taken. The temperature of the suspension was also measured with a thermometer and recorded appropriately. A blank cylinder was prepared with 50% calgon solution made up to the 1L mark with distilled water. Blank hydrometer readings at 40 seconds and 2 hours were obtained as previously described. Particle sizes were then calculated from equations (5, 6, 7, 8).
\[ \% \text{Silt} = \frac{\text{corrected ads reading} - \text{blank reading}}{\text{weight of soil used}} \times 100 - \% \text{clay} \quad (7) \]

\[ \% \text{Sand} = 100 - (\% \text{clay} + \% \text{silt}) \quad (8) \]

**Determination of organic matter:** The classical Walkley-Black rapid oxidation method was used for the determination of organic matter content\[^{16}\]. 0.1g of mud-wasp nest was weighed out and transferred to a 250 mL conical flask. Using a pipette, 10 mL aqueous 0.167 M K2Cr2O7 solution was added to the solution in the conical flask and swirled gently. 20mL portion of concentrated H2SO4 was then added and the mixture swirled gently to mix. Excessive swirling was avoided to prevent organic particles from adhering to the sides of the flask out of the solution. The contents of the flask were allowed to stand for 30minutes by placing it on a sheet of asbestos to avoid rapid heat loss. The content of the flask was then titrated against 0.5M ferrous ammonium sulphate solution (FAS). As end point was approached, the colour of the solution gradually changed to greenish depending on the amount of unreacted dichromate. At this stage, FAS was added drop-wisely until a sharp colour change of wine red was attained to mark the end point, viewed against a white –tile background. Blank titrations were performed in the same manner without the mud-wasp nest. Percent carbon and percent organic matter were calculated using equations (9) and (10).

\[ \% \text{oxidizable organic carbon,} \]

\[ \% C = \frac{B - S}{\text{milliequivalent weight of carbon}} \times 100 \]

where \( B = \) volume (mL) of Fe\(^{2+}\) solution used to titrate blank, \( S = \) volume (mL) of Fe\(^{3+}\) solution used to titrate sample, \( \frac{16}{40} = \) milliequivalent weight (g) of carbon

Oxidizable organic carbon was converted to total carbon by dividing by 0.77\[^{19}\]

\[ \% \text{Organic matter} = \% C \times 1.08 \]

**Spectrophotometric analysis of Hymenoptera spheciaed (mud-wasp) nest:** X-ray fluorescence (XRF) analysis: The fine powder material was pelletized and the solid pellet was then fed into a thermo 9900 intellipower x-ray fluorescence spectrophotometer for analysis.

**Fourier transforms infrared (FTIR) analysis:** FTIR data were collected on a Shimadzu FTIR-8400s Fourier Transform Infrared Spectrophotometer. Measurements were carried out in the range of 4000-200 cm\(^{-1}\).

**Powder x-ray diffraction (PXRD) analysis:** Powder x-ray diffraction data of Hymenoptera spheciaed nest were obtained on a Bruker D8 diffractometer using Cu \( k_\alpha \) (1.5406Å) radiation, over 2θ-range between 5\(^{\circ}\)- 90\(^{\circ}\) using a step size of 0.014\(^{\circ}\) and step time of 0.2s.

**Results and Discussion**

**Physicochemical characteristics of Hymenoptera spheciaed (mud-wasp) nest:** Results of the physicochemical properties of *Hymenoptera spheciaed* are presented in table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.54 ± 0.02</td>
</tr>
<tr>
<td>Abrasion resistance (%)</td>
<td>95.10 ± 0.10</td>
</tr>
<tr>
<td>Bulk density (g/cm(^3))</td>
<td>1.27 ± 0.02</td>
</tr>
<tr>
<td>Porosity (mg/g)</td>
<td>0.96 ± 0.01</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>1.29 ± 0.10</td>
</tr>
<tr>
<td>Total surface charge (mmolH(^+)eq/g)</td>
<td>1.35 ± 0.02</td>
</tr>
<tr>
<td>Iodine adsorption number (IAN) (mmol/g)</td>
<td>0.16 ± 0.20</td>
</tr>
<tr>
<td>Total surface area (g/mgI(_2))</td>
<td>6.33 ± 1.60</td>
</tr>
<tr>
<td>Organic matter (%)</td>
<td>4.77 ± 1.60</td>
</tr>
<tr>
<td>Particle size distribution :</td>
<td></td>
</tr>
<tr>
<td>% clay</td>
<td>10.96 ± 0.50</td>
</tr>
<tr>
<td>% silt</td>
<td>15.52 ± 3.37</td>
</tr>
<tr>
<td>% sand</td>
<td>73.52 ± 2.83</td>
</tr>
<tr>
<td>Cation exchange capacity (meq/100g)</td>
<td>0.15 ± 0.01</td>
</tr>
</tbody>
</table>

The pH value of 6.54±0.02 for *Hymenoptera spheciaed* (mud-wasp) nest indicated that the material is acidic. Generally, for pH-sensitive adsorbates, adsorbent pH in the range of 6-8 is acceptable for most adsorption applications in aqueous phase media\[^{16}\]\[^{20}\]. On the other hand, adsorbents, particularly those derived from agricultural residues have indicated an optimum metal ion uptake level at pH > 4.0 \[^{15}\]. Previous studies\[^{15}\]\[^{16}\] have shown that adsorbents are capable of increasing or decreasing the pH of slurries to levels that are out of range for metal ion adsorption.

The percent abrasion resistance also known as attrition is an indicator of the mechanical strength of an adsorbent for aqueous phase applications. It describes the ability of the adsorbent to, not only maintain its physical integrity during the adsorption process but also its ability to withstand frictional forces imposed by back washing\[^{16}\]. Previous investigations have revealed that for an adsorbent, particularly the low-cost ones to be considered for economic purposes, it should possess not only impressive adsorption properties, but a high resistance to abrasive forces in batch and column applications\[^{16}\]. Low abrasion resistance leads to loss of adsorbent particle integrity and formation of dust particles, resulting in the reduction in the rate of filtration, and in the amount of the adsorbent\[^{16}\]. Percent attrition for mud-wasp nest determined was 95.10±0.10%, a value interpretive of good mechanical strength, implying its potential for low degradability during handling.

Bulk density is one of the parameters that describe the quality of an adsorbent. It predicts the filterability of an adsorbent. High values of bulk density portend good quality adsorbents\[^{21}\]. The investigated mud-wasp nest has a bulk density value of
1.27±0.02 g/cm³, a comparatively high value with regard to other adsorbents reported in literature²,¹³,¹⁶.

Porosity of an adsorbent is a measure of the void in the adsorbent; and the greater the porosity of given adsorbent, the greater would be the relative size of molecules it can adsorb onto its crystal structure. Thus, the ion exchange or adsorption characteristics of adsorbent are determined also by the size and geometry of its pore spaces. In this study, mud-wasp nest has porosity of 0.96±0.01, which shows great promise for adsorption applications.

The amount of moisture present in the mud-wasp nest was determined to be 1.29±0.10%, a value far lower than 50.00% upper limit for adsorbents²². This implies that the mud-wasp nest can be stored for long periods without significant microbial activity being observed.

The adsorption capacity of an adsorbent is influenced by the presence of surface functional groups¹⁶. Surface functional groups that dominate adsorption behaviour of an adsorbent include carbonyls, carboxyls, phenolics, lactones, etc.²²,²³. These impart not only polarity onto the surface of the adsorbent, enhancing adsorption of charged species, but also influence possible mechanisms for covalent bonding and surface catalysis. The total surface charge for mud-wasp nest determined was 1.35±0.02mEqH⁺/g, which is comparable with values that have been reported for some adsorbents including commercial grade carbons²².

Iodine adsorption number (IAN) is a fundamental parameter usually used to characterize the performance of an adsorbent.²⁴ IAN value for mud-wasp nest was 0.16±0.20mmol/g, which is comparatively lower than reported for other adsorbents²². This implies that further treatment of mud-wasp nest will be desirable to enhance its adsorptive capacity.

Surface area of an adsorbent usually measures the extent of pore surface developed within the matrix of the adsorbent. Its value indicates the functionality of an adsorbent based on the principle that the greater the surface area, the higher the number of available adsorption sites¹⁶. A large surface area is therefore, a necessary requirement for a good adsorbent. When the internal pore structure of a material is highly developed the surface area is large, presenting the material as adsorbent and imparting in it the ability to adsorb gases and vapors from gas streams and dissolved/ dispersed substances from liquid media²⁴,²⁵. The investigated mud-wasp nest gave the total surface area value of 6.33±1.60g/m³, which compares with values reported for other effective adsorbents¹⁶,¹⁹.

CEC of soil (meqH⁺/100g) is a measure of the amount of sites on the soil surface that can retain cations through electrostatic force means. Cations retained by electrostatic means can easily be exchanged with other cations present and available in the soil environment²⁶. Sites for cation exchange are found mainly on clay and organic matter (OM) surfaces. In this investigation, the CEC for mud-wasp nest was 0.15±0.01meq H⁺/100g. Normal CEC ranges in soils have been reported to be from 3meq H⁺/100g for sandy soils low in organic matter to >25meq H⁺/100g for soils high in certain types of clay or OM²⁶. The cation exchange capacities of alkaline soils are commonly higher than those of acidic soils with comparable soil textures. This is due to two primary factors namely, the high CEC associated with the constant charges on 2:1 type clays that are most common in alkaline soils; and the even higher CEC resulting from the pH dependent charges on the humus colloids at these pH levels²⁶.

Mineral composition of Hymenoptera sphecidae (mud-wasp) nest: X-ray fluorescence analysis: XRF analysis of Hymenoptera sphecidae nest revealed that silica and alumina were present in dominant quantities of 26.5995%, and 10.5095% respectively (table 2). Calcium oxide, magnesium oxide and iron (III) oxide recorded values of 3.406%, 3.7015% and 2.3715% respectively. Trace amounts of sodium and potassium oxides were recorded as 0.9675% and 0.3010% respectively.

Fourier Transform Infrared (FTIR) analysis: Heating the KBr in the oven at 120°C was to prevent the broad spectral peak due to free OH groups from seriously affecting the interpretation on the bound hydroxyls associated, with any of the minerals²⁰. Absorption of infrared energy by a mineral is associated with the vibrational and rotational motion of molecules within it²⁴. The infrared spectrum obtained for Hymenoptera sphecidae nests is presented in figure 1. Quartz, feldspar, kaolinite and montmorillonite were identified from the absorption frequencies in the spectrum.

Quartz is one of the world’s most abundant minerals and an important component in the earth’s crust. It is primarily silicon dioxide, SiO₂²⁷. Strong IR absorption bands appeared at 795.91cm⁻¹ and 694.17cm⁻¹ suggesting the presence of quartz in the sample²⁷. The absorption band observed at 694cm⁻¹ was assigned to Si-O symmetrical bending vibrations²⁰,²⁷ while the band at 795.91cm⁻¹ indicated the presence of Si-O symmetrical stretching vibrations.

<table>
<thead>
<tr>
<th>Table-2</th>
<th>Mineral composition of hymenoptera sphecidae (mud - wasp) nest</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>SiO₂</td>
</tr>
<tr>
<td>% w/w</td>
<td>26.5995</td>
</tr>
</tbody>
</table>
Feldspar is an important group of rock-forming minerals with a general formula $WZ_4O_8$ where $W$ may be Na, K, Ca or Ba while $Z$ is Si and/or Al, the Si:Al ratio ranging from 3:1 to 1:1. Feldspar group of minerals have been analyzed by IR technique and reported. The sharp IR absorption peak appearing at 538.99 cm$^{-1}$ was assigned to feldspar and is due to Si-O asymmetric bending vibrations and Si-O-Al stretching vibrations, which often pertain to the 540-535 cm$^{-1}$ region of the IR spectrum.

Kaolin is a mineral with chemical composition $Al_2Si_2O_5(OH)_4$. It is a layered silicate mineral with one tetrahedral sheet linked through oxygen molecules to one octahedral sheet of alumina. Intense IR absorption bands appearing at 3697.99 cm$^{-1}$, 3661.91 cm$^{-1}$, 3621.33 cm$^{-1}$, 1034.14 cm$^{-1}$, 1100.14 cm$^{-1}$, 1008.09 cm$^{-1}$ and 470.68 cm$^{-1}$ in the spectrum indicated the presence of kaolinite. The strong absorbance at 3697.15 cm$^{-1}$ was assigned to inner surface OH stretching vibrations, while the band observed at 3697.15 cm$^{-1}$ was attributed to inner OH stretching vibrations indicating hydroxyl linkage. The absorbance at 1100.12 cm$^{-1}$, 1008.09 cm$^{-1}$ and 1034.14 cm$^{-1}$ were indicative of anti-symmetric Si-O-Si stretching vibrations, while the band at 470.68 cm$^{-1}$ was due to Si-O and Si-O-Fe stretching vibrations.

Montmorillonite is one of the very soft and tender phyllosilicate minerals. It is primarily hydrated magnesium calcium aluminium silicate (Mg, Ca) $OAl_2O_3.5SiO_2.nH_2O$ with $n$ ranging from 5 to 7. From the spectrum in figure 1, the presence of the broad IR absorption bands at 3436.52 cm$^{-1}$ and 1634.11 cm$^{-1}$ indicated the presence of montmorillonite. The band at 3436.52 cm$^{-1}$ was assigned to H-O-H stretching of absorbed water molecules, while the strong band at 1634.11 cm$^{-1}$ suggested OH deformation of water.

**Figure-1**

Infrared spectrum for *hymenoptera sphecidae* (mud-wasp) nest

**Powder X-ray diffraction (PXRD) analysis:** Qualitative mineralogy of *Hymenoptera sphecidae* nests was further tested by PXRD analysis. The x-ray diffractogram for the sample is presented in figure 2. The PXRD pattern of the sample when compared against the ICCD database for the theoretical phases shows that the dominant mineral present in mud-wasp nest is quartz (92.71%, pattern number = 01-087-2096), while halloysite7A-$Al_2Si_2O_5(OH)_4$ (pattern number = 00-029-1487) and halloysite10A-$Al_2Si_2O_5(OH)_4.2H_2O$ (pattern number = 00-029-1489) are present as 47.70% and 13.86% respectively. Halloysite is a 1:1 alumino silicate clay mineral and like kaolinite, it has a single layer structure. The primary difference between halloysite and kaolinite is their structure. Halloysite has a fibrous structure while kaolinite has a plate structure.

Because of the fibrous habit of halloysite, crystals are not oriented in basal parallel fashion. This results in weak 001 (hkl) reflections that are generally broad and strong non-basal reflections between 20°-30° 2θ; as a result, halloysite has a diffraction pattern with broad 001 and strong asymmetrical hkl reflections. Primary and secondary quartz were observed in the peak locations at 26.5° (d-space =4.251 Å) and 20.9° (d-space = 4.251 Å) respectively, while tertiary and quaternary quartz were identified at peak locations of 50.0-50.9° (d-space =1.817 Å) and 60.0° (d-space =1.541 Å) respectively.
Conclusion

Physicochemical characteristics of Hymenoptera sphecidae (mud-wasp) nest were investigated and values obtained compared favorably with those of other adsorbents previously studied by other researchers. XRF data revealed that SiO₂ and Al₂O₃ were the major minerals present, while Fe₂O₃, CaO and MgO were present in minor quantities. Na₂O and K₂O were however found to be present in trace amounts. From FTIR absorption peaks obtained, the constituent minerals identified were quartz, feldspar, kaolinite and montmorillonite. The dominant presence of quartz was further confirmed by PXRD which also revealed the presence of halloysites. Therefore, Hymenoptera sphecidae nest is a composite material, which may have very promising application in adsorption studies.

Acknowledgements

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