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NATURAL CLAY MINERAL-PERIWINKLE ACTIVATED CARBON COMPOSITE: CHARACTERISATION AND STRUCTURAL INSIGHT

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ABSTRACT

The intricacies of a natural clay mineral-periwinkle shell activated carbon (NM-PAC) composite were examined using Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), BET surface area analysis, and Fourier Transform Infrared spectroscopy (FTIR). TEM analysis revealed irregular shaped particles with sizes of around 100 nm and relatively good distribution characteristics. Further examination with SEM supported these findings, showing a heterogeneous microstructure with activated carbon particles evenly distributed within the clay matrix. This uniform distribution was indicative of a high surface area available for adsorption. BET surface area analysis of the NM-PAC was determined to be 72.243 m^2/g. FTIR analysis highlighted the presence of characteristic absorption bands related to the vibrational and rotational states of various functional groups. The broad band in the range of 3700–3000 cm^{-1} indicated the stretching vibration of hydroxyl groups, and new bands around 1730 cm^{-1}, 1250 cm^{-1}, and 1040 cm^{-1}, suggested the presence of carbonyl, carboxyl, and phenol groups respectively. These findings provide valuable insights into the composite's structural properties and its potential for improved adsorption efficiency, particularly for the removal of polar pollutants.

INTRODUCTION

The continuous growth of industrial activities and urbanization has increased the demand for clean water, air, and effective waste management solutions. Traditional methods for water purification and adsorption include activated carbon (AC), ion exchange resins, and membrane filtration (Bhatnagar *et al*., 2013). However, these methods have limitations, such as high production costs and environmental concerns. Consequently, there is a growing interest in developing new materials that are cost-effective, sustainable, and efficient for adsorption applications (Zhang *et al*., 2019).

Natural clay mineral-activated carbon composites (NM-AC) have recently emerged as a promising solution for adsorption applications. These composites combine the adsorptive properties of activated carbon with the benefits of natural clay minerals, such as enhanced mechanical stability, improved adsorption capacity, and eco-friendliness (Foo and Hameed, 2010). The synergistic effect of these materials has the potential to provide a more effective and sustainable solution for various adsorption applications.

Activated carbon (AC) is a widely used adsorbent in various applications, such as water purification, air filtration, and industrial waste management. It is derived from carbonaceous materials like coal, coconut shells, and wood through a high-temperature activation process. AC possesses a high surface area, porous structure, and surface functional groups, which contribute to its high adsorption capacity (Ahmad *et al*., 2014, Shaibu, *et al*., 2017). However, AC has certain limitations, including high production costs, the need for periodic regeneration, and environmental concerns related to its disposal (Foo and Hameed, 2010). These drawbacks have led to the search for alternative materials that can overcome these limitations.

Natural clay minerals have been investigated as potential adsorbents due to their abundance, low cost, and eco-friendly nature. Examples of these minerals include zeolites, clay minerals, and metal oxides (Wang and Peng, 2010). Some natural clay minerals exhibit high adsorption capacities for specific contaminants, such as heavy metals and organic pollutants (Motsi *et al*., 2009). However, natural clay minerals also have limitations, such as low adsorption capacities for a wide range of contaminants and insufficient mechanical stability (Foo and Hameed, 2010). This has led researchers to explore the potential of combining natural clay minerals with activated carbon to form composite materials with improved adsorption properties.

Several studies have been conducted on the synthesis and characterization of NM-AC for adsorption applications. For example, Zhang *et al*. (2019) prepared a composite of zeolite and activated carbon for the removal of methylene blue, finding that the composite exhibited enhanced adsorption capacity compared to either zeolite or activated carbon alone which is similar to Shaibu *et al*. (2014) report using a nanocomposite for methylene blue sequestration. In another study, Foo and Hameed (2010) synthesized a composite of clay minerals and activated carbon, demonstrating that the composite had improved mechanical stability, adsorption capacity, and regeneration potential. These findings highlight the potential of NM-AC as an effective adsorbent for various applications. The development of NM-AC offers several benefits over traditional adsorbents. Firstly, the use of natural clay minerals in the composite reduces the overall production cost, making it more economically viable for large-scale applications (Foo and Hameed, 2010). Secondly, the incorporation of natural clay minerals enhances the mechanical stability of the composite, which can improve its durability and reduce the need for frequent replacement (Zhang *et al*., 2019).

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Moreover, NM-ACs have been shown to exhibit improved adsorption capacities compared to either activated carbon or natural clay minerals alone, due to the synergistic effect of the two components (Zhang *et al*., 2019). This could lead to more effective removal of a wide range of contaminants, including heavy metals, organic pollutants, and pathogens, from water and air sources. The use of natural clay minerals in the composite makes it more eco-compatible in comparison to traditional adsorbents, as it reduces the environmental impact associated with the production and disposal of activated carbon (Motsi *et al*., 2009). This is particularly important in the context of global efforts to reduce pollution and promote sustainable development. Natural clay mineral-activated carbon composites represent a promising solution for various adsorption applications, offering improved performance, cost-effectiveness, and eco-friendly features compared to traditional adsorbents.

In this study, natural clay mineral was composted with periwinkle shell activated carbon and the structural and mechanical properties were elucidated. Characterising NM-PAC's morphology and structural properties is crucial to understanding their behavior and enhance their functionality.

MATERIALS AND METHODS

Natural clay mineral was sourced from Akwa Ibom state with huge deposit likewise the empty periwinkle shell. Deionized water was used for the preparation of solutions. All chemicals were of analytical grade and used without further purification.

Preparation of activated carbon from periwinkle shell

The production of activated carbon from periwinkle shell involved several stages. The first step involved washing the shells to remove impurities, followed by drying at 110 °C for 24 hours. The dried shells were then subjected to a two-stage process: carbonization and activation. Carbonization was done at high temperatures (500-600°C) for several hours, resulting in a carbonaceous material (Njoku, *et al*., 2015) followed by chemical activation. The chemical activation involved impregnating the carbonized material with phosphoric acid followed by heating (600-900 °C) (Foo and Hameed, 2012). The activated material is then washed, dried, and sieved to obtain the final product, activated carbon.

Preparation of Natural clay mineral-Periwinkle Activated Carbon Composite (NM-PAC)

The NM-PAC was prepared by a wet impregnation method, as described by Zhang *et al*. (2019) with slight modifications. Briefly, 10 g of natural clay mineral was mixed with 10 g of activated carbon in a beaker. 50 mL of deionized water was added to the mixture, and the slurry was stirred continuously for 4 hours at room temperature. The mixture was then dried in an oven at 105°C for 12 hours. After drying, the composite was ground using a mortar and pestle to obtain a fine powder. The resulting NM-PAC was sieved through a 200-mesh sieve to obtain a uniform particle size and then stored in an airtight container for characterization.

Characterization of NM-PAC

The morphology and microstructure of the prepared NM-PAC were analyzed using transmission electron microscopy (TEM) and scanning electron microscopy (SEM) (Foo and Hameed, 2010). The sample (NM-PAC) was made to be ultra-thin (less than 100 nm) to allow electron transmission. The sample was embedded in resin and ultra-microtomed to obtain thin sections. These sections are then placed on copper grids for TEM analysis. The sample preparation was a crucial step in the SEM analysis. The NM-PAC was first dried at a moderate temperature (~60-80°C) for several hours to remove moisture. Once dried, the sample was mounted onto a SEM stub using a conductive adhesive (like carbon tape or silver paint) to ensure electrical conductivity. Because activated carbon is non-conductive, the sample is then sputter-coated with a thin layer of a conductive material, such as gold or palladium, to prevent charging under the electron beam. The sample was loaded into the SEM chamber, and the chamber was evacuated to create a vacuum. An electron beam is scanned across the sample surface, and the emitted signals (secondary electrons, backscattered electrons) are captured by detectors. These signals were processed to produce a detailed image of the sample surface. The specific surface area, pore size, and pore volume were determined by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption-desorption isotherms (Ahmad *et al*., 2014). The NM-PAC was subjected to nitrogen gas adsorption at liquid nitrogen temperature (-196°C) using a gas adsorption analyzer. Before the analysis, the sample was outgassed under vacuum at 300°C for several hours to ensure the removal of any physically adsorbed substances on the surface. As regards the FTIR analysis, the NM-PAC was ground grinding the sample into a fine powder. The powdered sample is mixed with a suitable spectroscopic grade salt like potassium bromide (KBr). This mixture was ground uniformly and then compressed under high pressure to form a transparent pellet. The transparent nature of the pell*et al*lows the IR radiation to pass through it. The pellet was placed in the sample holder of the FTIR spectrometer. The instrument was then set to scan over a particular range of wavelengths, typically from 4000 to 400 cm^{-1}. The IR radiation is passed through the sample, and the transmitted light is recorded.

RESULTS AND DISCUSSION

Transmission electron microscopy of NM-PAC

The distribution of the of the natural clay mineral on the surface of the periwinkle shell activated carbon is shown in Figure 1.

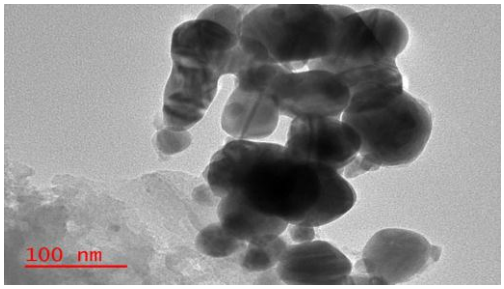

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Fig. 1: Size, shape and particle distribution of NM-PAC

TEM, by virtue of its high resolution, enabled detailed visualization of the NIM-PAC structure at the nanoscale. A typical analysis involves preparing thin sections of the composite using focused ion beam milling or ultramicrotomy, ensuring the sections are electron-transparent (Zheng *et al*., 2019). The TEM analysis revealed the NM-PAC's overall morphology, including particle shape, size, and distribution. It shows that the shape of the NM-PAC's particles was majorly irregular with sizes around 100 nm and relatively good distribution characteristics. (Bhattacharya *et al*., 2016). The TEM observed intercalation exfoliation of clay layers, crucial for assessing composite synthesis success. Furthermore, the dispersion and adherence of activated carbon within the clay matrix is believed to influence the composite's adsorption characteristics and mechanical properties.

Scanning Electron Microscopy

The SEM image of clay-activated carbon composites in Figure 2, typically revealed a heterogeneous microstructure with activated carbon particles embedded within the clay matrix. The size, shape, and distribution of these particles as supported by TEM analysis provided valuable information about the NM-PAC's adsorption capacity and mechanical properties. Importantly, a uniform distribution of small activated carbon particles suggested a high surface area available for adsorption. Evidence about the clay matrix was also deduced from the image. Smooth, continuous regions was observed suggesting a well-consolidated clay matrix, which can contribute to the composite's mechanical stability couple with apparent cracks in the matrix. This is similar to the observation of Shaibu *et al*. (2014) and Shaibu *et al*. (2022).

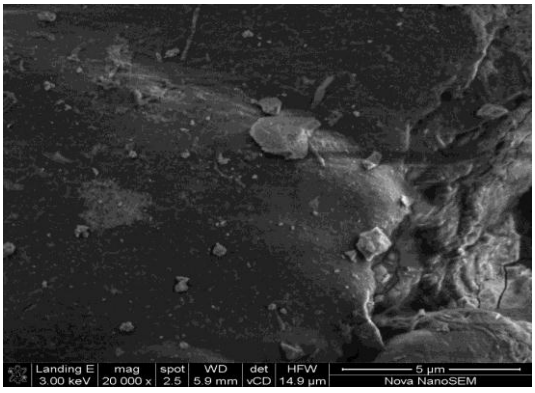

Figure 2: Surface morphology of NM-PAC

BET surface area analysis of NM-PAC

The adsorption data was then analyzed using the BET method, which assumes multilayer adsorption and uses the data collected in the low relative pressure (P/P0) region (0.05 to 0.35). The linear form of the BET equation was used to plot (V/(1-P/P0)) against P/P0. The slope and intercept of the resulting plot were used to determine the monolayer adsorbed gas volume (Vmon) and the BET constant (C). The BET surface area of the NM-PAC was found to be 72.243 m^2/g significantly higher compared to the individual components as reported by Shaibu *et al*. (2022), indicating that the composite formation had enhanced the porosity and surface area with a pore size of 95 **Å.** This characteristic makes the composite material more advantageous for adsorption applications. The BET surface area analysis provided valuable insights into the surface properties of the NM-PAC, Fig. 3. The enhanced surface area of the composite material indicated its potential for improved adsorption efficiency, underlining the significance of composite materials in environmental remediation applications (Udousoro *et al*., 2015), Shaibu *et al*., 2014 and Shaibu *et al*., 2022).

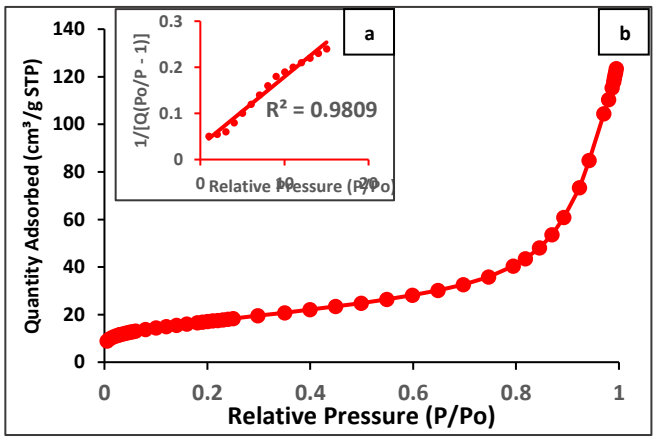

Figure 3: Nitrogen adsorption-desorption isotherm of NM-PAC

Table 1.0: Surface area and pore size analysis NM-PAC

Materials	BET surface area (m^2/g)	Pore size (Å)	Pore vol (cm^3/g)
NM-PAC	72.243	95.112	0.3009

Functional group analysis of NM-PAC

FTIR is a spectroscopic technique that provides information on the vibrational and rotational states of chemical bonds within a material. As such, it can be employed to identify functional groups and monitor chemical changes within the composite (Stuart, 2004). The NM-PAC FTIR spectrum displayed several characteristic absorption bands. The broad band in the range of 3700–3000 cm^{-1} was attributed to the stretching vibration of hydroxyl (OH) groups, common in both kaolinite and activated carbon (Murray, 2000; Rouquerol *et al*., 2013). The presence of this band confirmed the retention of hydrophilic properties, which are beneficial for adsorption applications. The peak around 1630 cm^{-1} was often associated with the deformation vibration of water molecules adsorbed on the surface of the composite (Madejová, 2003). This indicates the hygroscopic nature of the composite, an important consideration for storage and usage. Absorption bands around 1110 cm^{-1}, 1030 cm^{-1}, and 1000 cm^{-1} were indicative of the symmetric and asymmetric

stretching vibrations of Si-O and Al-O in the kaolinite structure (Frost *et al*., 2001). Upon activation of the carbon, changes were observed in the FTIR spectrum, reflecting the formation of additional functional groups. This might include the appearance of new bands around 1730 cm^{-1}, which can be attributed to carbonyl groups (C=O), or bands around 1250 cm^{-1} and 1040 cm^{-1}, associated with carboxyl (COOH) and phenol (OH) groups, respectively (Rouquerol *et al*., 2013). The introduction of these oxygen-containing functional groups improves the adsorption capacity of the composite. The FTIR spectra revealed critical details about the surface chemistry and structural alterations of the NM-PAC, which directly influence its adsorption capacity. For instance, the emergence and increase in intensity of the bands related to oxygen-containing groups (e.g., C=O, OH) implied increased polarity of the composite surface. This increased polarity can enhance the adsorption of polar pollutants, thereby improving the overall efficiency of the NM-PAC's for pollutant removal.

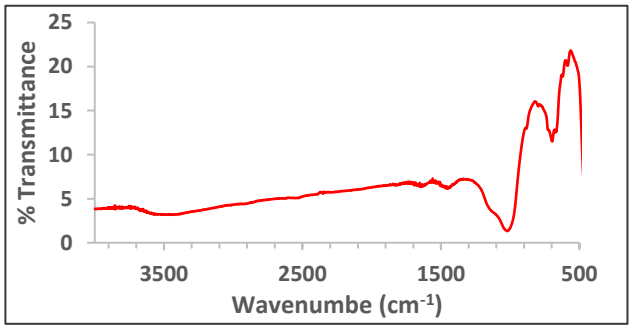

Figure 4: Fourier transform infra-red spectrum of NM-PAC

CONCLUSION

The study used various analytical techniques to evaluate the structural properties and potential adsorption capacity of natural clay mineral-periwinkle shell activated carbon (NM-PAC). TEM and SEM analyses revealed a heterogeneous microstructure with a well-distributed and irregularly shaped activated carbon particles embedded within the clay matrix. The composite's BET surface area was determined to be significantly higher than its individual components, indicating an enhanced porosity advantageous for adsorption applications. FTIR analysis identified the presence of several functional groups, and changes in the spectrum upon carbon activation implied an increased surface polarity, enhancing the NM-PAC's overall efficiency for polar pollutant removal.

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