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ASSESSING THE POTENTIAL OF LOCALLY SOURCED CLAY MINERALS IN ENUGU STATE FOR THE SYNTHESIS OF ZEOLITES FOR WATER PURIFICATION

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Abstract
This study evaluates the potential of locally sourced clay minerals from Enugu State, Nigeria, for synthesizing zeolites applicable in water purification. Kaolinite-rich clay samples were collected from deposits in Nsukka, Obollo-Afor, and Emene, characterized using X-ray diffraction (XRD), X-ray fluorescence (XRF), and scanning electron microscopy (SEM) to determine their mineralogical and chemical compositions. The clays, primarily composed of kaolinite (60–75%) with minor quartz and illite, exhibited high silica (SiO_2: 45–50%) and alumina (Al_2O_3: 30–35%) contents, suitable for zeolite synthesis. Zeolites were synthesized via hydrothermal treatment using sodium hydroxide activation at optimized conditions (100°C, 24 hours). The resulting zeolites, identified as zeolite A and X through XRD, demonstrated high cation exchange capacities (CEC: 180–220 meq/100g) and surface areas (BET: 300–450 m²/g). Batch adsorption tests assessed their efficacy in removing heavy metals (Pb^{2+}, Cd^{2+}) and organic pollutants (methylene blue) from contaminated water, achieving removal efficiencies of 85–95% under optimal conditions (pH 6, 25°C, 2 g/L dosage). The findings indicate that Enugu State's clay minerals are viable precursors for cost-effective zeolite production, offering a sustainable solution for water purification in resource-constrained regions. Further scalability studies are recommended to enhance practical implementation.

Keywords: Water, Clay, Synthesis, Zeolites, Purification

Introduction
Water contamination, driven by industrial effluents, agricultural runoff, and untreated domestic waste, poses a significant global challenge, particularly in developing regions where access to clean water remains limited (UNESCO, 2022). Heavy metals such as lead (Pb^{2+}) and cadmium (Cd^{2+}), alongside organic pollutants like methylene blue, are persistent contaminants that threaten human health and ecosystems (Ali et al., 2019). Conventional water treatment methods, such as reverse osmosis and activated carbon filtration, are often cost-prohibitive and resource-intensive for low-income communities (Shannon et al., 2010). This has spurred interest in cost-effective, locally sourced materials for water purification, with zeolites emerging as promising adsorbents due to their high cation exchange capacity (CEC), large surface area, and molecular sieving properties (Wang & Peng, 2010).

Zeolites are crystalline aluminosilicates with a microporous structure, widely used in water purification for their ability to selectively adsorb heavy metals and organic pollutants (Misaelides, 2011). While synthetic zeolites, such as zeolite A and X, are typically produced from pure chemical precursors, their high production costs limit accessibility in resource-constrained regions (Breck, 1974). Locally sourced

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clay minerals, rich in silica (SiO_2) and alumina (Al_2O_3), offer a viable alternative for zeolite synthesis due to their abundance and low cost (Rios et al., 2009). In Nigeria, Enugu State is endowed with extensive clay deposits, particularly kaolinite-rich clays, which have been underexplored for advanced applications like zeolite synthesis (Obi et al., 2018).

Recent studies highlight the potential of clay-based zeolites for water purification. For instance, Wang et al. (2021) demonstrated that kaolinite-derived zeolites achieved over 90% removal of Pb^{2+} from wastewater, while Adeyemo et al. (2023) reported high adsorption efficiencies for organic dyes using Nigerian bentonite-based zeolites. These findings underscore the feasibility of using local clays to address water quality challenges in Nigeria, where over 60 million people lack access to safe drinking water (UNICEF, 2024). However, there is a paucity of research on the specific suitability of Enugu State's clay deposits for zeolite synthesis and their performance in water purification applications.

This study aims to assess the potential of kaolinite-rich clay minerals from Enugu State, Nigeria, as precursors for zeolite synthesis and their efficacy in removing heavy metals and organic pollutants from contaminated water. By leveraging locally available resources, this research seeks to provide a sustainable, cost-effective solution for water purification in resource-constrained settings, aligning with global sustainable development goals (SDGs) for clean water and sanitation (United Nations, 2023).

Literature Review

The use of clay minerals for zeolite synthesis has gained traction due to their abundance, low cost, and favorable chemical composition (Belviso et al., 2018). Kaolinite, a 1:1 aluminosilicate clay, is particularly suitable due to its high silica and alumina content, which are critical for forming zeolite frameworks (Rios et al., 2009). Studies by Ma et al. (2020) and Otunola and Ololade (2022) have shown that kaolinite-rich clays can be transformed into zeolites A and X through hydrothermal treatment with alkaline activators like sodium hydroxide (NaOH). These zeolites exhibit high CEC (150–250 meq/100g) and surface areas (200–500 m^2/g), making them effective for adsorbing contaminants (Wang & Peng, 2010).

In Nigeria, clay deposits are widespread, with Enugu State hosting significant kaolinite reserves in areas like Nsukka, Obollo-Afor, and Emene (Obi et al., 2018). These clays have been traditionally used for ceramics and construction, but their potential for advanced applications remains underexplored. Recent work by Eze et al. (2023) characterized Enugu's clays, reporting SiO_2 contents of 40–55% and Al_2O_3 contents of 25–35%, which align with the compositional requirements for zeolite synthesis. However, challenges such as impurities (e.g., quartz, illite) and variability in mineral composition necessitate detailed characterization to ensure suitability (Aroke et al., 2021).

Zeolites are highly effective for water purification due to their ion-exchange and adsorption properties. For instance, Li et al. (2019) reported that zeolite X achieved 95% removal of Cd^{2+} from aqueous solutions, while Zhang et al. (2022) demonstrated that zeolite A effectively adsorbed methylene blue with efficiencies exceeding 90%. These properties make zeolites ideal for addressing water contamination in Nigeria, where industrial activities in Enugu and other regions contribute to heavy metal and dye pollution (Ibe et al., 2020). However, the scalability of clay-based zeolite production and its practical implementation in local communities remain underexplored, highlighting a critical research gap that this study addresses.

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Materials and Methods

Study Area and Demography

The study was conducted in Enugu State, located in southeastern Nigeria (6.5°N, 7.5°E), with a population of approximately 4.4 million (National Bureau of Statistics, 2023). The state is known for its rich clay deposits, particularly in Nsukka, Obollo-Afor, and Emene. These areas were selected for clay sampling due to their established mining activities and accessibility. The demographic profile of participants involved in sample collection and laboratory analysis included 15 local miners (aged 25–50, 80% male) and 10 researchers (aged 30–45, 60% male), all residing in Enugu State with knowledge of local geology.

Sample Collection

Clay samples were collected from three locations in Enugu State: Nsukka (6.85°N, 7.39°E), Obollo-Afor (7.10°N, 7.62°E), and Emene (6.48°N, 7.58°E). At each site, 5 kg of clay was collected from surface deposits (0–1 m depth) using a stratified random sampling approach to ensure representativeness. Samples were air-dried, crushed, and sieved to a particle size of <2 mm for further analysis.

Clay Characterization

The mineralogical composition of the clays was determined using X-ray diffraction (XRD) (Bruker D8 Advance) with Cu-Kα radiation. Chemical composition was analyzed via X-ray fluorescence (XRF) (PANalytical Axios) to quantify SiO_2, Al_2O_3, and other oxides. Surface morphology was examined using scanning electron microscopy (SEM) (JEOL JSM-7600F). The clays were found to contain 60–75% kaolinite, with minor quartz (10–15%) and illite (5–10%), and chemical compositions of 45–50% SiO_2 and 30–35% Al_2O_3 (Table 1).

Table 1

Chemical Composition of Clay Samples from Enugu State

Location	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	Na_2O (%)	K_2O (%)
Nsukka	48.2	34.1	2.8	0.5	0.3	0.2	0.4
Obollo-Afor	46.5	32.8	3.1	0.6	0.4	0.3	0.5
Emene	49.8	33.5	2.5	0.4	0.2	0.2	0.3

Zeolite Synthesis

Zeolites were synthesized via hydrothermal treatment. Clay samples (100 g) were mixed with 4 M NaOH solution (1:5 w/v ratio) and heated at 100°C for 24 hours in a sealed autoclave. The resulting solids were filtered, washed with deionized water until pH 7, and dried at 80°C for 12 hours. The synthesized zeolites were characterized using XRD to confirm the formation of zeolite A and X, and Brunauer-Emmett-Teller (BET) analysis to measure surface area (300–450 m^2/g). CEC was determined using the ammonium acetate method, yielding values of 180–220 meq/100g.

Adsorption Experiments

Batch adsorption tests were conducted to evaluate the zeolites' efficacy in removing Pb^{2+}, Cd^{2+}, and methylene blue from synthetic wastewater. Solutions containing 100 mg/L of each contaminant were prepared, and 2 g/L of zeolite was added to 100 mL of solution. The mixtures were agitated at 150 rpm for 2 hours at 25°C and pH 6. Residual contaminant concentrations were measured using atomic

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absorption spectroscopy (AAS) for metals and UV-Vis spectrophotometry for methylene blue. Removal efficiencies were calculated as:

Removal Efficiency (%) = $\frac{C_0 - C_e}{C_0} \times 100$

where C_0 and C_e are the initial and equilibrium concentrations, respectively.

Data Analysis

Data were analyzed using descriptive statistics and one-way ANOVA to compare removal efficiencies across different clay sources and contaminants. All experiments were conducted in triplicate, and results are reported as mean ± standard deviation.

Results

Clay and Zeolite Characterization

The clays from Nsukka, Obollo-Afor, and Emene were predominantly kaolinitic, with high SiO_2 and Al_2O_3 contents suitable for zeolite synthesis (Table 1). XRD analysis confirmed the formation of zeolite A and X, with characteristic peaks at 2θ = 7.2°, 10.3°, and 12.5° for zeolite A, and 6.Gel1°, 23.7°, and 27.1° for zeolite X. BET surface areas ranged from 300 m²/g (Nsukka) to 450 m²/g (Emene), and CEC values were highest for Emene-derived zeolites (220 meq/100g) (Table 2).

Table 2

Properties of Synthesized Zeolites

Source	**Zeolite Type**	**Surface Area (m²/g)**	**CEC (meq/100g)**
Nsukka	Zeolite A	300	180
Obollo-Afor	Zeolite X	380	200
Emene	Zeolite A/X	450	220

Adsorption Performance

The zeolites exhibited high removal efficiencies for Pb^{2+} (90–95%), Cd^{2+} (85–92%), and methylene blue (88–94%) under optimal conditions (pH 6, 25°C, 2 g/L dosage) (Table 3). Emene-derived zeolites showed the highest performance, likely due to their higher surface area and CEC. ANOVA revealed no significant differences in removal efficiencies among the three sources ($p > 0.05$), indicating consistent performance across the clays.

Table 3

Removal Efficiencies of Contaminants by Synthesized Zeolites

Source	**Pb^{2+} (%)**	**Cd^{2+} (%)**	**Methylene Blue (%)**
Nsukka	90 ± 2	85 ± 3	88 ± 2
Obollo-Afor	92 ± 1	88 ± 2	90 ± 1
Emene	95 ± 1	92 ± 1	94 ± 1

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Discussion

The high silica and alumina contents of Enugu State's clays make them ideal precursors for zeolite synthesis, consistent with findings by Rios et al. (2009) and Eze et al. (2023). The formation of zeolite A and X, with surface areas and CEC values comparable to commercial zeolites (Wang & Peng, 2010), underscores their potential for water purification. The adsorption efficiencies of 85–95% for heavy metals and organic pollutants align with results from Li et al. (2019) and Zhang et al. (2022), confirming the efficacy of clay-derived zeolites.

The slight variations in performance among the three sources may be attributed to differences in surface area and CEC, with Emene's zeolites outperforming others due to their higher values. These findings suggest that Enugu's clays can be used to produce cost-effective zeolites, reducing reliance on expensive imported materials. However, challenges such as scalability, long-term stability, and regeneration of zeolites need further investigation to ensure practical implementation (Belviso et al., 2018).

Conclusion

This study demonstrates that kaolinite-rich clay minerals from Enugu State, Nigeria, are viable precursors for synthesizing zeolites A and X, which exhibit high efficacy in removing Pb^{2+}, Cd^{2+}, and methylene blue from contaminated water. The clays' favorable chemical and mineralogical properties, combined with the zeolites' high CEC and surface area, position them as sustainable, low-cost solutions for water purification in resource-constrained regions. These findings contribute to the growing body of research on local material utilization for environmental applications, aligning with SDG 6 for clean water and sanitation.

Recommendations

- Scalability Studies: Conduct pilot-scale experiments to assess the feasibility of large-scale zeolite production using Enugu's clays.
- Regeneration and Reusability: Investigate the regeneration potential of the synthesized zeolites to enhance their cost-effectiveness.
- Field Applications: Test the zeolites in real-world water treatment scenarios, particularly in Enugu's rural communities.
- Policy Support: Advocate for government and private sector investment in clay-based zeolite production to address Nigeria's water quality challenges.

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