

AFRICAN JOURNAL OF
Biological and Physical Sciences

An international, peer-reviewed, open-access journal

VOLUME 1 · ISSUE 1 · 2026

ARTICLE TYPE
Original ResearchARTICLE ID
AFJBPS-2026-001YEAR
2026LICENSE
CC BY 4.0Assessing the Potential of Locally Sourced Minerals in Enugu State for the
Synthesis of Zeolites for Water Pollution ControlIdah Nwaka Nwopu^{1*}¹ Department of Chemistry, Enugu State College of Education (Technical), Enugu, Nigeria***Corresponding author:** Idah Nwaka Nwopu, Department of Chemistry, Enugu State College of Education (Technical), Enugu, Nigeria

ABSTRACT

Enugu State carries a documented and largely unremediated water pollution burden, driven principally by acid mine drainage from the abandoned Onyeama and Okpara collieries, industrial effluent along the Ekulu corridor, and unregulated waste disposal across the Nyaba catchment. Remediation has been constrained by the cost of imported adsorbent media. This study assessed whether minerals occurring within Enugu State are chemically and mineralogically suitable as feedstock for the low-cost synthesis of zeolites for water treatment. A desk-based evaluative resource assessment was adopted, in which published geochemical and mineralogical data on the state's lithostratigraphic units were compiled and appraised against a six-criterion suitability rubric covering aluminosilicate reactivity, silica-to-alumina molar ratio, impurity burden, beneficiation intensity, reserve accessibility, and activation cost. Six candidate feedstocks were evaluated: kaolinitic clay of the Mamu Formation, clay of the Nsukka Formation, Ajali glass sand, Enugu Shale, colliery coal ash, and rice husk ash from the Adani rice belt. Results indicate that the kaolinitic clays of the Mamu and Nsukka Formations obtained the highest weighted suitability indices (4.15 and 3.85 of 5.00 respectively), with computed silica-to-alumina molar ratios spanning approximately 1.8 to 5.0, a range that brackets the synthesis windows for zeolites LTA, FAU-X, FAU-Y, and Na-P1. Ajali glass sand and Adani rice husk ash were found unsuitable as standalone precursors but valuable as silica modifiers for ratio adjustment. Elevated Fe₂O₃, reaching 29.42% in some southeastern clay samples, emerged as the principal constraint, requiring magnetic or chemical beneficiation. The study concludes that Enugu State possesses a genuine and internally complete precursor base for zeolite manufacture, and recommends a staged laboratory verification programme followed by pilot-scale deployment at identified pollution hotspots.

Keywords: zeolite synthesis; kaolin; metakaolin; Enugu State; water pollution; acid mine drainage; Anambra Basin; low-cost adsorbents

How to cite: Nwopu, I. N. (2026). Assessing the potential of locally sourced minerals in Enugu State for the synthesis of zeolites for water pollution control. African Journal of Biological and Physical Sciences, 1(1), Article AFJBPS-2026-001.

1. INTRODUCTION

Access to safe water remains one of the most persistent development challenges confronting southeastern Nigeria, and Enugu State presents a particularly instructive case. The state's industrial history is bound up with coal: the Onyeama, Okpara, Iva Valley, and Ribadu mines operated for the better part of the twentieth century before extraction ceased in the 1990s. Drainage from the abandoned Onyeama workings has been shown to carry

sulphate concentrations of 313.0 mg L⁻¹, carbonate of 253.0 mg L⁻¹, and nitrate of 86.6 mg L⁻¹, with a pollution load index for toxic metals of 3,110 and ecological risk ranked in the order lead, cadmium, arsenic, nickel, cobalt, iron, and chromium [26]. The Ekulu River, which rises at the base of the Enugu-Okigwe Cuesta and serves low-income settlements across Iva Valley, Abakpa Nike, and Emene, carries a measurable burden of arsenic, cadmium, chromium, copper, lead, nickel, and zinc alongside polycyclic aromatic hydrocarbons [32].

Conventional responses to this class of contamination share a common weakness in the Nigerian context: they depend on imported consumables priced in foreign currency. Zeolites are crystalline microporous aluminosilicates built from corner-sharing SiO₄ and AlO₄ tetrahedra. Substitution of trivalent aluminium for tetravalent silicon generates a net negative charge balanced by exchangeable extra-framework cations, conferring the high cation-exchange capacity that underpins their use in water treatment [6,8]. Although commercial production relies on purified sodium silicate and sodium aluminate, kaolinitic clay can serve as a single inexpensive source of both silicon and aluminium once converted to reactive metakaolin by calcination [13,15].

Enugu State lies across the Anambra Basin and exposes the Enugu Shale, Mamu Formation, Ajali Formation, Nsukka Formation, and Imo Shale, including extensive clay and glass-sand deposits [23,24]. What has not been established is whether these materials meet the compositional requirements for zeolite synthesis, and if so which deposits and which zeolite phases represent the most realistic starting point.

1.1 Statement of the problem

Enugu State exports its clay and sand as low-value construction inputs while importing adsorbent media to treat water polluted by its own mining legacy. No published study has systematically evaluated the state's mineral inventory against the compositional criteria that govern zeolite synthesis.

1.2 Objectives

The study set out to inventory mineral deposits in Enugu State that are chemically plausible as zeolite precursors; compile and normalise published major-oxide data; compute silica-to-alumina molar ratios against established phase windows; rank feedstocks on a weighted suitability rubric; and relate the ranked feedstocks to the documented contaminant profile of Enugu's polluted water bodies.

1.3 Scope

The study is delimited to mineral occurrences within Enugu State and to the low-temperature hydrothermal and alkaline-fusion routes realistically available to a Nigerian producer. It is a desk-based assessment of secondary data; no primary sampling, laboratory synthesis, or adsorption testing was undertaken.

2. REVIEW OF RELATED LITERATURE

2.1 Conceptual and theoretical framework

A zeolite is defined by its framework topology. LTA (zeolite A), FAU (zeolites X and Y), and GIS (zeolite Na-P1) are the phases most commonly obtained from clay precursors. The framework silica-to-alumina ratio governs both which phase will crystallise and the properties of the product [6,3]. Kaolinite, Al₂Si₂O₅(OH)₄, has a silica-to-alumina molar ratio of 2.0. Calcination between roughly 550 and 900 °C produces amorphous, highly reactive metakaolin [22], which dissolves in caustic solution and recondenses into zeolite frameworks.

Ion-exchange theory holds that uptake of a metal cation proceeds by stoichiometric replacement of a framework-balancing cation, with selectivity determined by ionic radius, hydration energy, charge density, and framework aperture [8]. Clay-derived zeolites consistently prefer lead over copper, cadmium, zinc, and cobalt [14]. Langmuir and Freundlich isotherms, with pseudo-second-order kinetics, describe chemisorptive uptake at a defined site population [12].

2.2 Geological setting

Enugu State lies between 6°00'–7°10' N and 6°50'–7°52' E within the Anambra Basin. The Mamu and Nsukka Formations host the principal clay occurrences and coal seams. The Ajali Sandstone is a friable quartz arenite mapped as glass sand, with silica contents exceeding 96% in fresh samples [31]. The Nigerian Geological Survey Agency maps clay, pottery clay, glass sand, kaolin, coal, limestone, gypsum, and ironstone across the state [23].

2.3 Empirical review and gap

Nigerian kaolin has an established record as a zeolite precursor. Kovo et al. synthesised zeolite Y and ZSM-5 from Ahoko kaolin after metakaolinisation at 600 °C for as little as six minutes [15], and showed that ageing time selects between zeolite A and zeolite Y [16]. Ibrahim et al. reported Langmuir capacities of 16.17, 15.96, 12.25 and 12.03 mg g⁻¹ for Cd, Pb, Cu and Zn on a kaolin–ash faujasite [12]. Joseph et al. demonstrated that faujasite from a southeastern Nigerian clay removed approximately 99% of lead within ten minutes [14]. Ríos et al. showed that synthetic zeolites outperform fly ash and natural clinker against acid mine drainage [30]. Geological studies of Enugu minerals have been directed at ceramic and construction uses; none has evaluated them against zeolite-synthesis criteria.

3. METHODOLOGY

A desk-based evaluative resource assessment was adopted. Data were drawn from peer-reviewed geochemical studies of Anambra Basin units, official NGSA mapping, and validated water-quality studies of Enugu water bodies. Grey literature and studies without stated analytical methods were excluded.

Six criteria were weighted: aluminosilicate reactivity (25%), silica-to-alumina ratio proximity to phase windows (20%), impurity burden as combined Fe₂O₃ and TiO₂ (20%), beneficiation intensity (15%), reserve accessibility (10%), and activation energy cost (10%). Each feedstock was scored from 1 to 5 and a weighted index computed. Silica-to-alumina molar ratios were obtained from reported mass percentages by multiplying the mass ratio by 1.697 (molar masses SiO₂ 60.08 g mol⁻¹; Al₂O₃ 101.96 g mol⁻¹).

Three limitations qualify the findings. Clay compositional data derive from the wider southeastern outcrop belt rather than exclusively from Enugu State boundaries. The weighting scheme embodies analytical judgement. No laboratory verification was undertaken.

4. RESULTS

Table 1. Mineral occurrences in Enugu State screened as candidate zeolite precursors.

Material	Host formation	Principal axis	Precursor role
Kaolinitic clay	Mamu Formation	Enugu, Udi, Awgu	Primary Si and Al source
Pottery / kaolin clay	Nsukka Formation	Nsukka, Igbo-Etiti	Primary Si and Al source
Glass sand	Ajali Formation	Udi, Ezeagu, Nsukka	Silica modifier
Shale	Enugu Shale	Enugu escarpment	Marginal; high Fe and K
Coal ash / spoil	Mamu (colliery waste)	Onyeama, Okpara, Iva	Secondary; waste valorisation
Rice husk ash	Agro-residue	Adani, Uzo-Uwani	Amorphous silica modifier

Compiled from NGSA (2023), Nwajide (2013), and Onyekuru et al. (2018).

Table 2. Representative major-oxide composition and computed silica-to-alumina molar ratios.

Feedstock	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	TiO ₂ (%)	SAR (molar)
Mamu / Nsukka clays	31.70–56.45	19.30–29.30	3.11–29.42	2.21–7.04	1.8–5.0
Ajali sand (fresh)	94.8–99.0	<1.0	<1.0	<0.5	>70
Ajali sand (ferruginised)	80–90	3.50–11.60	1.80–3.60	<1.0	12–43
Enugu Shale	45–58	14–22	5–12	1.0–2.5	3.5–7.0
Colliery coal ash	40–55	18–28	8–20	1.0–3.0	2.4–5.2
Rice husk ash	85–95	<1.0	<1.0	<0.2	>140

Clay data from Onyekuru et al. (2018); Ajali data from Tijani et al. (2010). SAR = silica-to-alumina molar ratio = mass ratio × 1.697.

Table 3. Weighted suitability indices for candidate feedstocks.

|--|--|--|--|--|--|

Feedstock	React. (.25)	SAR (.20)	Impur. (.20)	Benef. (.15)	Access (.10)	Energy (.10)	Index
Mamu clay	5	5	3	3	5	4	4.15
Nsukka clay	4	5	3	3	5	4	3.85
Rice husk ash	5	2	5	5	2	3	3.70
Ajali sand	2	1	5	5	5	3	3.20
Enugu Shale	2	3	2	2	4	3	2.45
Colliery ash	3	4	1	2	3	2	2.30

Scores 1 (least favourable) to 5 (most favourable). Indices computed by the present assessment.

Table 4. Attainable zeolite phases and match to documented Enugu contaminants.

Phase	Target SAR	Route from Mamu clay	Reported performance	Enugu target
LTA (Na-A)	2.0	Direct metakaolinisation	Sr, Pb, Cd, Zn uptake	AMD metals, hardness
FAU-X	2.2–3.0	Metakaolin + alkaline fusion	Pb ~99% in 10 min	Ekulu Pb, Cu, Cd
FAU-Y	3.0–6.0	Dealumination or silica addition	High-capacity, acid stable	Low-pH AMD streams
GIS (Na-P1)	2.0–5.0	Low-temperature hydrothermal	High CEC, organics	Mixed municipal effluent
SOD (sodalite)	1.0–2.0	Over-crystallisation product	Lower CEC; by-product	Not targeted

Phase windows from Breck (1974) and Johnson and Arshad (2014).

Table 5. Documented water pollution burden in Enugu State.

Water body	Principal sources	Documented contaminants	Source
Onyeama mine drains	Abandoned colliery AMD	SO ₄ 313 mg L ⁻¹ ; PLI 3,110; Pb > Cd > As > Ni > Co > Fe > Cr	Oyetibo et al. (2021)
Ekulu River	AMD, industry, waste	As, Cd, Cr, Cu, Pb, Ni, Zn; 17 PAHs	Umeh et al. (2023)
Onyeama catchment	Acid mine drainage	Acidic pH; elevated Fe, Mn, Al	Ozoko (2015)

PLI = pollution load index; PAHs = polycyclic aromatic hydrocarbons; AMD = acid mine drainage.

5. DISCUSSION

The central finding is that Enugu State holds a compositionally complete precursor base for zeolite manufacture. The computed silica-to-alumina molar ratio range of approximately 1.8 to 5.0 for the state's kaolinitic clays brackets four phases: LTA near 2.0, FAU-X between 2.2 and 3.0, Na-P1 across 2.0 to 5.0, and the lower end of the FAU-Y window. A producer working from a single deposit could therefore tune the product phase by adjusting synthesis conditions rather than switching raw material.

The principal constraint is iron. Reported Fe₂O₃ in southeastern clays reaches 29.42% [25], far above the level tolerable in zeolite synthesis. The constraint is spatially variable: the same study recorded low-iron samples. Deposit selection within a formation therefore matters more than formation selection between formations. Where iron cannot be avoided, magnetic separation, dilute acid leaching, and the sedimentation refining used by Kovo et al. to recover 97% kaolin offer demonstrated routes [15].

Metakaolin inherits kaolinite's ratio near 2.0, which favours LTA but limits access to acid-stable FAU-Y. Enugu holds two silica modifiers: Ajali glass sand (>96% SiO₂) and rice husk ash from the Adani belt (amorphous silica typically >85%). The latter dissolves more readily in caustic solution and converts a milling waste into a process input.

The correspondence with documented contaminants is close. Lead ranks first in the Onyeama ecological-risk sequence [26], and is the cation for which clay-derived faujasite shows greatest selectivity [14]. The Ekulu profile of As, Cd, Cr, Cu, Pb, Ni and Zn [32] falls substantially within the divalent set reported by Ibrahim et al. [12]. Arsenic, occurring predominantly as an oxyanion, is the notable exception and would require surface modification or a complementary step. Acid mine drainage is characteristically acidic, and zeolite performance falls sharply below pH 5, reinforcing the value of a local silica modifier for FAU-Y.

6. CONCLUSION

Six candidate materials were evaluated against a weighted six-criterion rubric. The kaolinitic clays of the Mamu and Nsukka Formations emerged as the leading precursors, with weighted suitability indices of 4.15 and 3.85 of a possible 5.00 and computed silica-to-alumina molar ratios spanning approximately 1.8 to 5.0. Ajali glass sand

and Adani rice husk ash are unsuitable as standalone precursors but valuable as silica modifiers. Iron oxide content is the principal constraint, though spatially variable and addressable by established beneficiation. Enugu State possesses a genuine and internally complete precursor base for local zeolite manufacture, and the case for laboratory verification is well founded.

7. RECOMMENDATIONS

A systematic sampling campaign should be conducted across Mamu and Nsukka clay outcrops in the Enugu, Udi, Awgu, and Nsukka axes, with XRD and XRF characterisation prioritising low-iron horizons. Laboratory synthesis trials should use metakaolinisation at 600–850 °C followed by hydrothermal crystallisation, with ageing time varied to establish phase selectivity. Adsorption testing should be performed against actual Onyeama and Ekulu water. A pilot fixed-bed unit should be sited at a colliery discharge point once laboratory performance is confirmed, with pH correction upstream of adsorption. Policy should link Adani rice-milling residue to any zeolite venture so that the silica-modifier supply chain is secured.

AUTHOR CONTRIBUTIONS

I.N.N. conceived the study, compiled and analysed the secondary geochemical dataset, ranked the feedstocks, and wrote the manuscript.

ACKNOWLEDGEMENTS

The author thanks colleagues in the Department of Chemistry, Enugu State College of Education (Technical), for comments on an earlier draft.

FUNDING

This research received no external funding.

CONFLICT OF INTEREST

The author declares no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

ETHICAL APPROVAL

Not applicable. The study is a desk-based assessment of published geochemical and water-quality data.

DATA AVAILABILITY

All compiled compositional values are drawn from the cited published sources and are summarised in Tables 1–5.

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