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Dissolution kinetics of coal and limestone samples from Kogi state, Nigeria

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Abstract

This work is concerned with the dissolution behaviour and kinetics of Okobo coal and Obajana limestone from Kogi State, Nigeria, within acidic, basic, and neutral media. This was achieved using hydrochloric acid and sodium hydroxide with distilled water, representing acidic, basic and neutral environment respectively, where the rates were determined for six hours. Overall, the dissolution rates were significantly enhanced under an acidic medium for both minerals, indicating a maximum dissolution of 6.1% for Okobo coal, as depicted in results, and 7.7% dissolution in the case of Obajana limestone. Basic media provided moderated dissolution, while the water had minimum effects. The kinetic analysis using zero-order and Higuchi models indicated that the zero-order best fitted coal dissolution in acidic condition, but for limestone, both the models were fitted very well. These results would provide a good knowledge to the mineral industry, environmental management, and building industries through the conditions of favoring mineral decomposition and utilization.

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1. Introduction

The organic material in the coal which is derived through the process of coalification is basically made up of large polymeric molecules in which chemical structures are variable and non- repetitive. However, the properties of coal appear to be dependent mainly on the physical and chemical structure of these organic compounds. The mineral matter may exist both as mineral species and as mineral phases of widely-varying particle sizes and also as species that are chemically built up by the organic matter. It is hoped that the physical structure of coal is represented by spatial arrangement of large complex molecules, along with a few much smaller ones which may be affected by either acidic, basic or neutral liquid media in the form of dissolution. The physical and chemical properties of coal depend upon its physical structure [1]. Coal extraction tends to lead to the release of more methane than was originally trapped within the mined coal seam itself, because the drop in pressure draws in additional gas from surrounding

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strata. Also, the mining process tends to fracture the surrounding strata including neighbouring seams, particularly where long wall extraction is used.

Chemical structures of organic molecule in coal vary greatly, especially with its rank, to the extent that coals even from the same region may likely show more differences than similarities.

Physical properties of coal generally vary so systematically with coal rank that it may likely be possible to reasonably predict the carbon content of the volatile matter of the coal [1].

Research has identified that coal dissolution behaviour is significantly controlled by its chemical and physical composition. The research of Lawrence *et al*. [2] on South African coal fly ash, emphasized the role of acidic and basic media in accelerating or moderating dissolution processes. Acidic solutions generally enhance the breakdown of the coal matrix as a result of protonation effects, which destabilize mineral bonds and lead to the release of metals and organic matter. Also, Okoro *et al*. [3] investigated the leaching behaviour of Okobo coal. They observed that the dissolution rates in acid conditions were higher compared to neutral and basic conditions, because of the breakdown of the coal matrix due to protonation effects.

Limestone was most popular in the late 19th and early 20th centuries. It is a sedimentary rock composed largely of the mineral calcite (calcium carbonate: $CaCO_3$). This calcite came from sea animal shells. It is also precipitated from ocean water. It often has variable amounts of silica in it, as well as varying amounts of clay, silt, and sand. Limestone is a white, chalky solid in most conditions. As a sedimentary rock, it will usually contain fossils of ancient creatures. It is used extensively in the construction industry, like in cement. It is used widely around the world as a building material. Limestone is popular in architecture, even the pyramids of Egypt are made of limestone. It makes up 10% of all sedimentary rocks on earth. It is partially soluble and reactive. It is easily dissolved by acids and it is a main ingredient of cement and mortar. Limestone is also used as a soil conditioner, in the manufacturing of glass, and in agriculture.

Limestone is of course a sinequanon in the manufacture of cement which is a very vital ingredient in the construction industry especially housing, bridges and factories [4]. Limestones show many differences in physical character. The physical character is usually a reflection of the chemical composition. Limestones vary in colour from pure white to black, depending on differences in their chemical composition. The amorphous and semi crystalline limestones are usually light grayish to bluish gray in colour, or brindled. In the highly crystalline limestones, the impurities may be crystallized and seperated in bands or the colouring matter may be uniformly or irregularly distributed throughout. Limestones also vary in texture from amorphous and semi- crystalline to crystalline. The variation in density and absorption properties are largely due to differences in texture. Simply put, limestones vary in hardness, specific gravity and compactness ranging from the unconsolidated shell marls to the crystalline marbles. Many varieties of limestone are named and classified on the basis of chemical composition, such as high-calcium, magnesium, dolomitie, etc. Due to their structure or most abundant accessory constituent, special names are also given as argillaceous, chalky, sillceous, bituminous, and pisolitic; and others are named from certain predominant fossils as crinoidal, coralline, and formaniferal [5].

Oliveira *et al*. [6] highlighted the chemical and mineralogical properties of limestone. Their study showed that in acidic conditions, the dissolution rate of limestone increased because of the carbon dioxide-releasing reaction and the further formation of soluble salts like calcium chloride. Dissolution properties are very important for the utilization of limestone in various industries, either for construction or in the manufacture of cement. According to Magaji *et al*. [7], chemical composition influences the reactivity of limestones and, thus, their suitability for various industrial uses.

The rates of mineral dissolution contribute to processes controlling soil fertility, porosity in aquifers and oil reservoirs, transport and sequestration of contaminants and CO_2, cycling of metals and formation of ore deposits, and many other geochemical characteristics and phenomena. Mineral dissolution thus influences the chemical and physical nature of the earth's landscape as well as the quality and quantity of portable water and fertile soil available to sustain ecosystems. The rates of mineral dissolution determine the lifetimes of mineral in soil environments. Also, investigation of mineral dissolution rate helps to promote quantitative prediction of the evolution of our environment. Mineral dissolution is largely dependent on its chemical composition and the dissolution process variables such as temperature, particle size, acid concentration, pH and solid- to-liquid ratio. That is; dissolution rate increases with increase in temperature and acid concentration, but decreases with increase in particle size, pH, and solid-to-liquid ratio [2].

The kinetic modeling is important to understand the dissolution rates and mechanisms involved. A study by Apua and Madiba [8] and Ezewna *et al*. [9], utilizing zero-order and Higuchi models, respectively, in studying mineral dissolution, proved the utility of the models in describing the release rates under varying conditions.

The primary concern about the presence of metals and heavy metals in drinking water and other consumables, are their objectionable tastes. The taste of these metals in consumables can be easily detected even at low concentrations of about 1×8 mg/L. Their availability depends on dissolution of the minerals and their subsequent leaching behaviour. There are many problems that result from toxicity emanating from dissolution of these minerals. These include anorexia, oligura, diarrhoea, hypothermia, diphasic shock, metabolic acidosis and even death.

Limestone (CaCO3) is a vital raw material in many processing industries such as water and waste water treatment, surface coats and paints, petroleum refining, chemical synthesis, fertilizer manufacture etc. One must also not omit the utilization of limestone as sorbents [6]. Also, dissolution characteristics of these minerals which greatly affect their adsorption capacity is sparsely documented.

Although much literature is available on dissolution kinetics, few studies were carried out with respect to adsorption capacity and the exact environmental implications as far as the dissolved minerals are concerned. Furthermore, most studies often research either



(a) (b)

Figure 1: (a) Okobo coal (b) Obajana limestone.

acidic or basic media without detailed comparative analysis involving neutral conditions. Such a gap leads to a limitation in full understanding of how these minerals behave under various real-life scenarios where neutral pH conditions might arise. Therefore, the study of the behaviour of these minerals, such as coal and limestone, in a wide range of acidic, basic and neutral environments is needed for better prediction of their dissolution patterns and environmental impacts. In this respect, addressing the above gaps would result in useful data on industrial applications and environmental management. Figure 1 shows samples of Okobo coal and Obajana limestone.

2. Materials and method

2.1. Reagents

Analytical grade reagents were used in this study. They include hydrochloric acid, sodium hydroxide, and distilled water. These were all be procured from certified vendor.

2.2. Equipment/instruments and apparatus

The equipment involved include thermometer, masking tape, digital pH meter (model PHS- 25), crusher, plastic container with a screw tap, hand gloves, filter paper, filtering funnel, polypropylene bag, refrigerator, hand trowel, clock. Instruments and apparatus employed includes routine laboratory glassware such as beakers, volumetric flask, test tubes, measuring cylinders, conical flask, pipettes, funnel, hot plates, weighing balance, filter paper, thermostatic vessel, platinum dishes.

2.3. Description of study areas

Coal was sampled from Okobo, a small town in Enjema District of Ankpa Local Government Area (eastern part) of Kogi State. The coal mining site is located on latitude 7^{o} 22’ ’ North; longitude 7^{o} 37’33” East. A GPS mapping of study area for coal is given in Figure 2. Obajana, the sampling area for limestone is a cement industrial town located in Lokoja Local Government area of Kogi State, Nigeria. Obajana is on the latitude 7^{o} 55’ North; longitude 6^{o} 26’0’ ’ East. It hosts Dangote Cement factory as result of the presence of abundant limestone which serve as raw materials for the factory. Figure 3 show the GPS map of the area.

2.4. Sampling

2.4.1. Coal sampling

The sampling procedure employed was the one adopted by Akinyeye *et al.* [10], with slight modifications. This was achieved by developing a sample grid across the Okobo mining site for coal collection. Precision was ensured such that samples was collected at equal intervals; for every 50 meters. This approach minimizes the risk of sampling bias and ensures the sample becomes representative of the whole site.

A gross sample of 60 g was obtained after the homogenization of the five samples. The sample was thoroughly washed, to remove extraneous materials such as dirt, sand and other impurities and subsequently dried and milled to fine particle sizes. The grinded coal was dried in an oven at 90 ^{0}C for 24 hours and later sieved with mesh of 350 μm particle size [11]. The sample residue was filtered using quartz-fibre filter (0.4 μm pore size) and then with Whatman filter paper. The sample residue was air dried in an oven at a temperature of 35^{o}C for 8 hours prior to analysis.

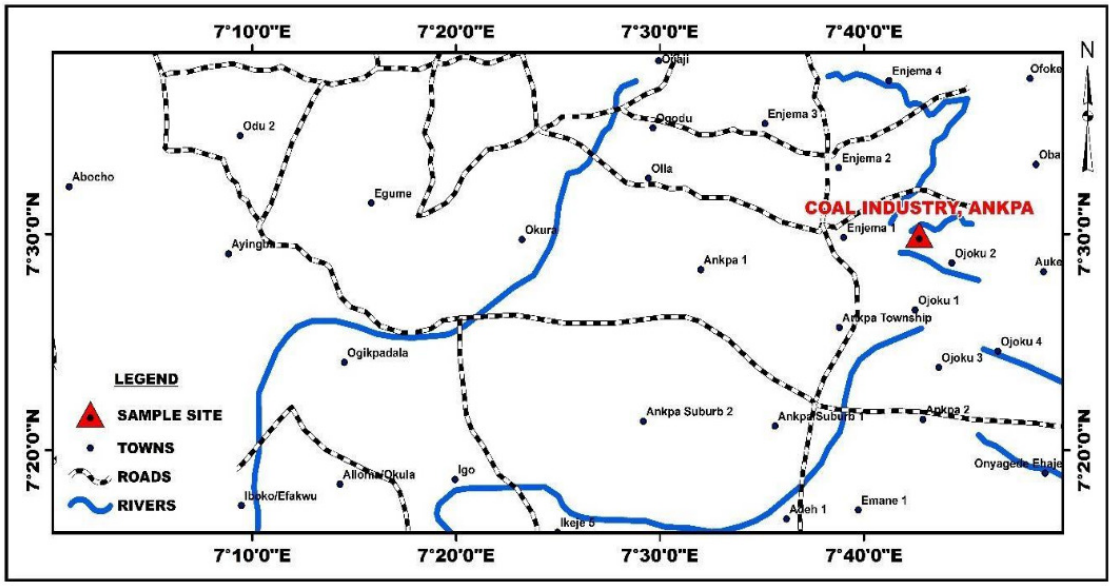


Figure 2: GPS map showing coal mining site at Okobo, Ankpa local government area, Kogi State.

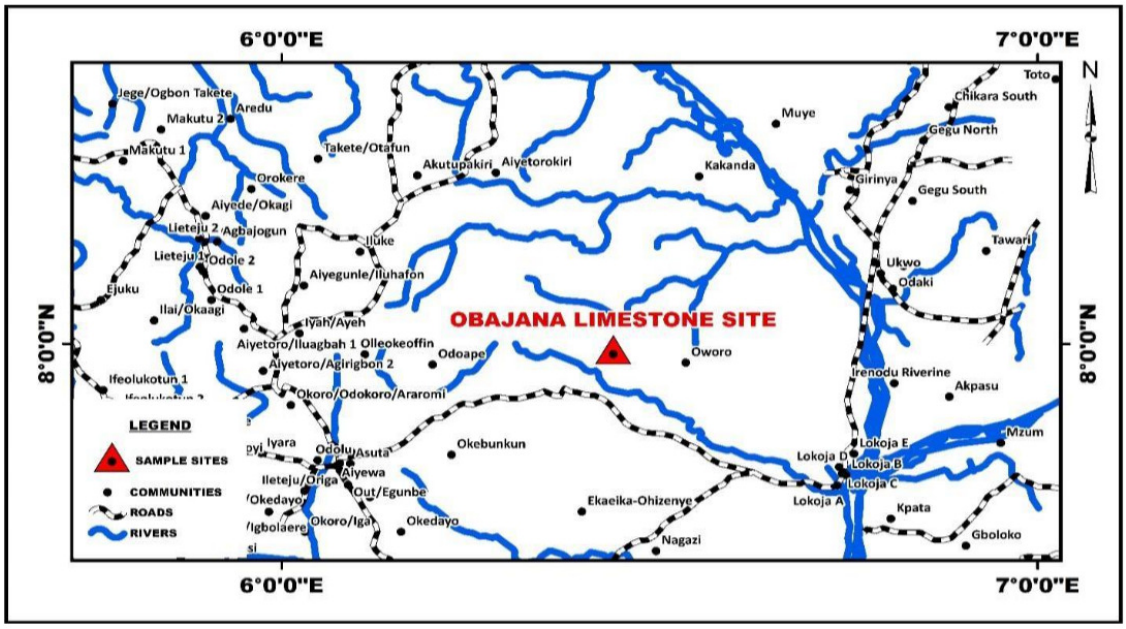


Figure 3: GPS map showing limestone mining site at Obajana, Lokoja local government area, Kogi state.

2.4.2. *Limestone sampling*

The random sampling at the Obajana limestone depot further guaranteed precision in that it did not look at location bias alone, since properties vary within such a limestone. For more precision, the method adopted by Haruna *et al.* [12] was followed by which several sub-samples-smaller samples of five 20 g coal samples were homogenized together to one composite sample. The limestone sample was crushed with the help of a mechanical crusher in the various quarry sites and collected into analytical bottles. The sample was also washed to remove surface impurities and air-dried at ambient temperature. The limestone sample was further milled into grain size of less than 2 mm mesh and stored in a desiccator prior to analysis [13].

2.5. *Preparation of standard solution*

This was done in line with the procedures reported by Nabil [14] by using the dilution formula ($M_1V_1 = M_2V_2$) to calculate the volume of 0.1 M concentrated HCl required. For 1 L of 0.1 M HCl, V_1 = 8.33 mL of concentrated HCl was diluted with distilled water to 1 L using a standard concentration of 12 M of the acid. In a similar way, four grams of NaOH was weighed and dissolve in

a small volume of distilled water. The solution was transferred to a 1 L volumetric flask and diluted to the mark with distilled water to prepare 1 L of 0.1 M NaOH [15].

2.6. Dissolution experiment (Gravimetry)

The dissolution kinetics of coal and limestone in acid and base were studied using method adopted by Akinyeye *et al.* [10]. One g of pulverized samples was added to the 6 reactor vessels containing 100 mL 0.1 M HCl and 0.1 M NaOH separately. The temperature, solid-to-liquid ratio, particle size and pH were kept at constant at stirring speed of 200 rpm for 1, 2, 3, 4, 5 and 6 hours. This was done using a temperature controlled magnetic stirrer. The sample was removed, filtered and dried in the oven and weighed till constant weight was obtained. Dissolution in distilled water was set as control experiment.

2.7. Control experiment

The dissolution experiments were conducted under controlled conditions: fixed temperature, pH, and solid-to-liquid ratios. This consistency ensures that differences in the dissolution rates observed are a function of the nature of the samples and not a product of variation in experimental setup. Also, replicate dissolution experimental runs at different times of 60, 120, 180, 240, 300, and 360 minutes were carried out to determine the precision in order to reduce random errors.

2.8. Quality assurance/control

In order to ensure the accuracy of the results, analytical standard reagents (hydrochloric acid and sodium hydroxide) were obtained to help in maintaining the level of precision in the experiment by reducing the probability of errors due to impurities. Similarly, instruments were calibrated and re-calibrated after each experimental run.

2.9. Dissolution kinetics

The following kinetic models were employed to assess the dissolution kinetics of the samples under investigation.

2.9.1. Zero-order model

Zero-order kinetics has been observed in acid media dissolution of carbonaceous materials for coal. Here, the dissolution rate is independent of the surface area of coal and availability of reactive solvent [16]. Similarly, such an assumption of zero-order kinetics can often be made in dissolution processes of coal and limestone and indeed in many cases when coal and limestones are subjected to acids and base either for chemical extraction or for environmental applications, because the concentration of calcium carbonate is not changing significantly over the course of reaction. This process of dissolving calcium carbonate in acid, such as HCl, base and neutral environment might be considered to occur at a constant rate if excess acid is present and the system is well-mixed [3].

Solid dissolution from dosage forms that do not disaggregate and release the substance slowly can be represented by the equation:

$$Q_0 - Q_t = K_0 t. \tag{1}$$

Rearrangement of equation (1) yields:

$$Q_t = Q_0 + K_0 t, \tag{2}$$

where Q_t is the amount of solid dissolved in time t, Q_0 is the initial amount of the substance in the solution (most of the times, $Q_0 = 0$) and K_0 is the zero order release constant expressed in units of concentration per time [17].

2.9.2. Higuchi model

Higuchi developed models to study the release of water soluble and low soluble substances incorporated in semi-solid and solid matrices. The Higuchi model can be applied for cases involving dissolution in which the involvement of a porous matrix takes place or the release of ions or solutes follows diffusion-controlled kinetics. Regarding the dissolution or leaching of minerals from coal, it can be controlled by the ion diffusing through the pores of the coal particle, thus allowing square root dependence of the release rate therefore, considering the model for perfect explanation of coal dissolution [16].

In the case of limestone, Higuchi model is considered to best explain limestone dissolution due to fact that dissolution process in acid and basic solutions can be regarded as a diffusion-controlled process in which the dissolution rate depends on some diffusive transport of ions across the boundary layer around the solid particle. This is particularly relevant when coarse particles or minerals of low solubility are dealt with [16].

To study the dissolution from a planer system having a homogeneous matrix, the relation obtained is shown in equation (3) [18].

$$Q = [D(2C - C_s)C_s t]^{1/2}, \tag{3}$$

where Q is the amount of substance released in time t per unit area, C is the initial substance concentration, C_s is the substance solubility in the matrix media and D is the diffusivity of substance molecules in the matrix substance.

In general Higuchi model can be simplified as:

$$Q = K_H t^{1/2}, \tag{4}$$

where, K_H is the Higuchi dissolution constant [16]. Higuchi describes substances release as a diffusion process based in the Fick's law, square root time dependent.

Table 1: Dissolution of coal in different media; acid and base (water as a control) as a function of time.

Media/Weight (g)		Time (min) 60	120	180	240	300	360	Mean ± SD
Acid	Wt_{Ai}	1.0026	1.0086	1.0043	1.0045	1.0050	1.0021	1.0045±0.002
	Wt_{Af}	0.9477	0.9527	0.9483	0.9433	0.9473	0.9526	0.9487±0.004
	Wt_{Ad}	0.0549	0.0557	0.0561	0.0612	0.0577	0.0495	0.0559±0.004
% diss A		5.4758	5.5225	5.586	6.0926	5.7413	4.9396	5.5596±0.4
Base	Wt_{Bi}	1.0033	1.0050	1.0100	1.0110	1.0035	1.0014	1.0057±0.004
	Wt_{Bf}	0.9460	0.9601	0.9275	0.9201	0.9377	0.9406	0.9387±0.014
	Wt_{Bd}	0.0573	0.0449	0.0822	0.0909	0.0658	0.0608	0.0669±0.017
% diss B		5.7112	4.4677	8.1386	8.9911	6.5571	6.0715	6.6562±1.65
Water	Wt_{Wi}	1.0059	1.0040	1.0059	1.0036	1.0034	1.0027	1.0043±0.001
	Wt_{Wf}	1.0039	0.9951	1.0010	0.9971	0.9985	0.9986	0.9990±0.003
	WtWd	0.0020	0.0089	0.0049	0.0065	0.0049	0.0041	0.0052±0.002
% diss W		0.1988	0.8865	0.4871	0.6477	0.4883	0.4089	0.51956±0.23

Key: Wt_A = Weight of Coal in Acid, Wt_B = Weight of Coal in Base, Wt_W = Weight of Coal in Water, Wt_{Xi} = Initial Weights, Wt_{Xf} = Final Weights and Wt_{Xd} = Difference in Weight between Initial and Final, % Diss X = Percentage Weight Dissolved, SD = Standard deviation.

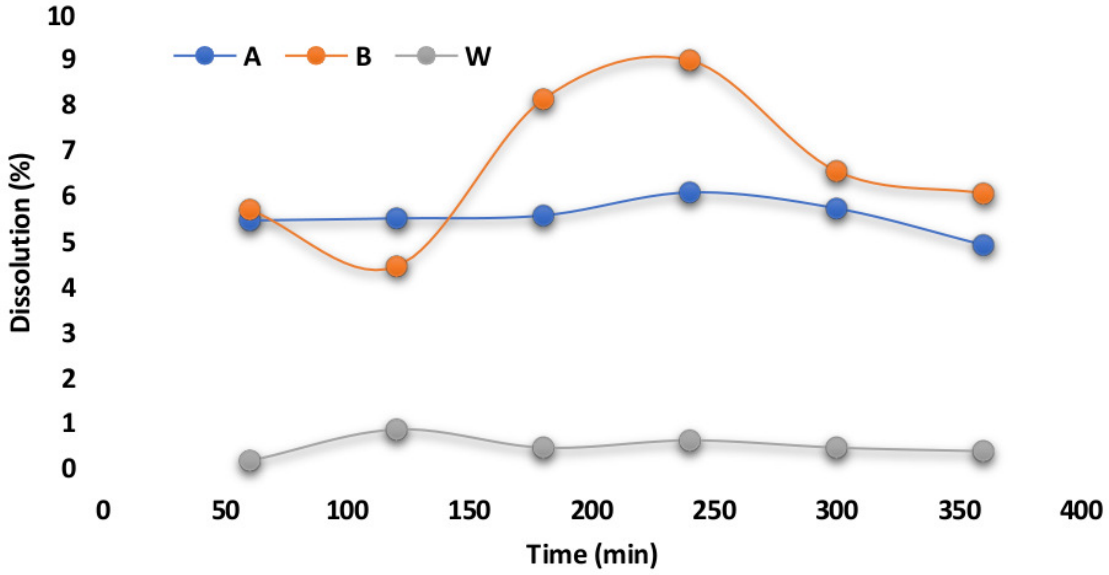


Figure 4: Dissolution profile of okobo coal in acid and base using water as control.

3. Results and discussion

3.1. Dissolution studies

Data presented in Table 1 (and plotted in Figure 4) show that Okobo coal exhibited a noticeable reduction in weight and percentage dissolve in the acidic media. After 240 minutes, the percentage dissolution reached its peak of 6.0926%. This suggests that the acid efficiently decomposes the coal matrix, providing way for different constituents to be released [2].

The disintegration of the organic and inorganic matrix of Okobo coal after protonation is the cause of the increased rate of dissolution in the acidic medium (with a value of 5.5596 ± 0.4 %). Acids have a reputation for violently breaking down mineral bonds, liberating metal ions and organic components in the process. This finding agrees with other research that shown that coal and coal fly ash dissolves similarly in acidic conditions [2].

In basic medium, Okobo coal sample dissolution as observed in Table 1, also received support in terms of weight loss (0.0669 ± 0.017 g) and percentage dissolution (6.6562 ± 1.65 %); after 240 minutes, the percentage dissolution reached 8.9911%. The capacity of the base to hydrolyze particular mineral components in the coal was demonstrated by the dissolution rate, which was considerably higher in the base than in the acid [3].

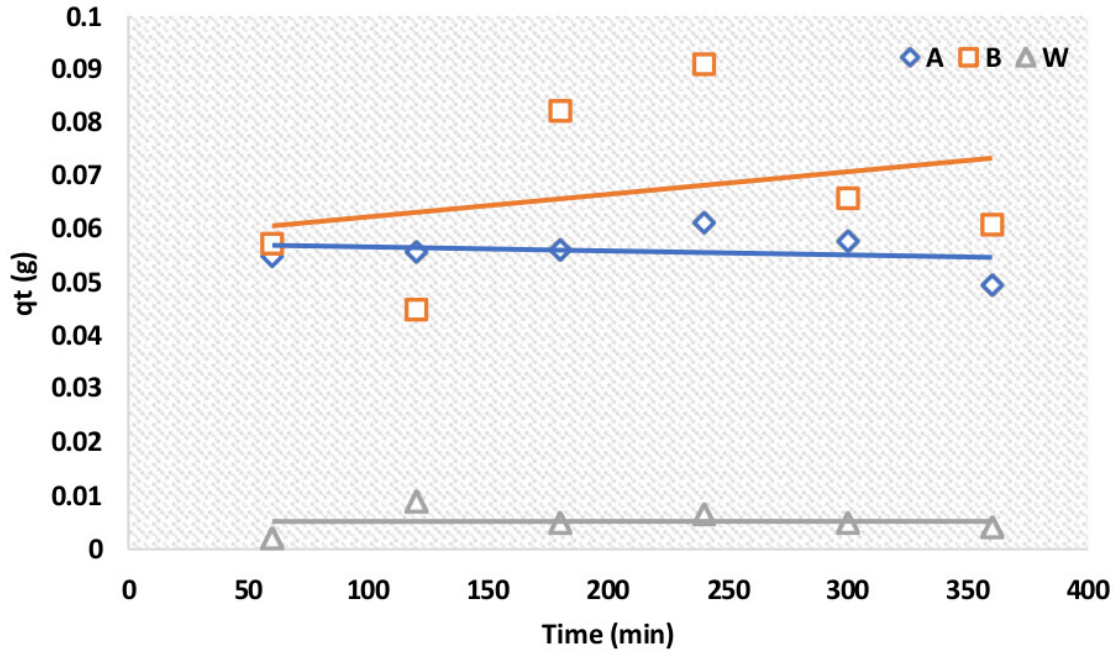


Figure 5: Zero order plots for dissolution kinetics of Okobo coal in acid (A), base (B) and water (W).

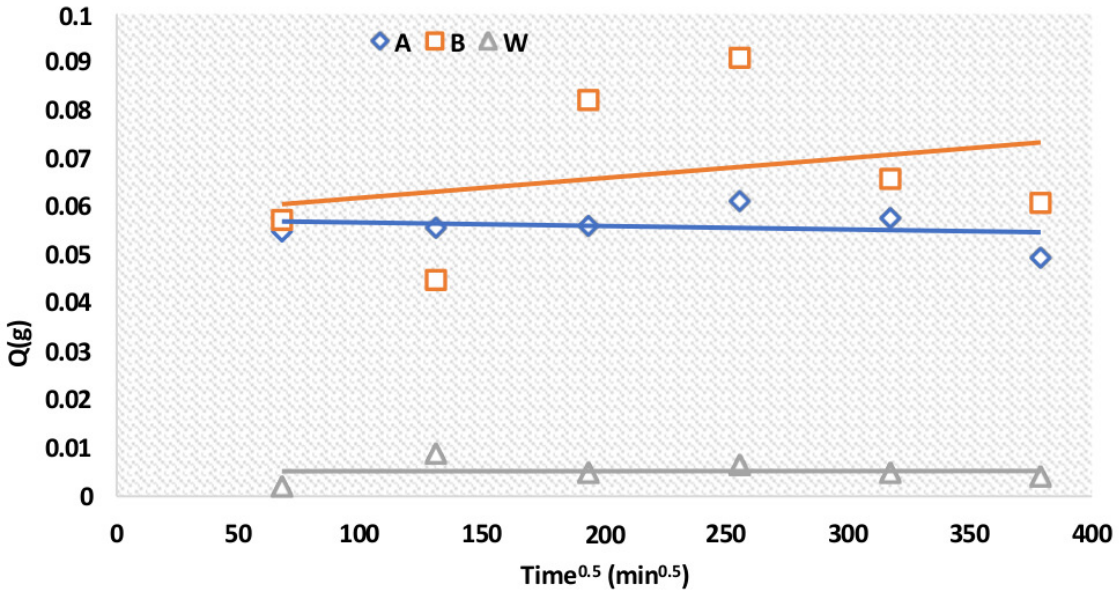


Figure 6: Higuchi plots for dissolution kinetics of Okobo coal in acid (A), base (B) and water (W).

The hydroxide ions in the basic media assist in the dissolution of coal by hydrolyzing certain minerals that are present in the coal. The observed dissolution and leaching characteristics of coal in alkaline solutions, is in agreement with [3]. When coal was dissolved in distilled water (Table 1), the maximum percentage dissolution reached after 240 minutes was 0.6477%. This brings up the topic of weight loss and percentage dissolution. This emphasizes that considerable coal dissolution requires a reactive but not neutral media [3].

As a control, distilled water exhibited very little dissolving power of 0.51956 ± 0.23 %. This suggests that coal dissolution is low in the absence of a reactive media, underscoring the significance of chemical reactivity in the dissolution process [3].

3.2. Dissolution kinetics modelling

The study of the kinetic model is crucial since they describe the rate of dissolution of Okobo coal in water, acid and base solutions [8], two reaction kinetic models were investigated for their suitability to describe the rate of dissolution process, the currently used

Table 2: Experimental constants and parameters for the dissolution of Okobo coal.

Dissolution model	Constants	Medium		
		A	B	W
Zero Order	R^2	0.0793	0.0492	5E-06
	kSC (g/min)	4E-05	-8E-06	5E-06
Higuchi Model	R^2	0.048	0.0805	3E-05
	kH ($g/min^{0.5}$)	-7E-06	4E-05	1E-07

Key: A=Acid, B=Base and W=Water

ones are: zero- order and Higuchi models.

3.2.1. Zero-order

i. The zero-order model fitted best in coal in acidic media, presenting the rate constant k0 = 4×10^{-5} g/min and value of 0.0793 (Table 2 and Figure 5). This indicates the generally linear dissolution rate when the concentration of the reactive solvent is high enough to maintain consistent breakdown within minerals. However, the low value of R^2 indicates that there is variation in the experimental results, which could possibly be because of heterogeneity in the composition of coal [2, 9].

ii. Basic Medium: The model fitted poorly under basic conditions, as deduced from the negative rate constant, k_0 = -7 $\times$ 10^{-6} g/min (Table 2), indicating possible mineral precipitation [3]. Thus, such a discrepancy could be explained based on the lower reactivity of basic media and the formation of some byproducts as insoluble salts.

iii. Neutral medium: The zero-order model was not effective (as shown in Table 2) in the case of neutral medium, which also agreed with the literature that the minimum chemical reaction occurs in the absence of significant pH changes [8].

The zero-order model fitted best in the media when obtaining an acid by a rate constant g/min and a value of 0.0793. This is relatively low, but nonetheless, the general trend in acidic environments where protonation facilitates the breakdown of the mineral matrix is such that a near-constant dissolution rate can be achieved for Okobo coal. This is evidenced by research

findings that show acids break mineral bonds, and hence create conditions favourable for a steady dissolution, in line with the findings of Ezenwa *et al.* [9] and Lawrence *et al.* [2]. The success of the zero-order model can perhaps be attributed to the high availability of hydrogen ions in the acidic conditions, ensuring constant interaction between the solution and the mineral surface that maintains a uniform reaction rate.

3.2.2. Higuchi model

Acidic and Basic Media: The Higuchi model in Table 2 (and plotted in Figure 6) gave a very poor fit in coal for both the acidic-R^2 = 0.048 and the basic-R^2 = 0.0805 media, indicating that the dissolution kinetics of coal was not diffusion-controlled. This also agrees with studies that porous matrix effect is negligible in non-homogeneous materials such as coal. It is in this respect that the poor fit in acid media may be related to the model's assumption of uniform diffusion, which does not account for the heterogeneous structure of coal [17].

Wang *et al.* [19] reported coal dissolution studies conducted in China and recorded an appreciable increase in the dissolution of coal upon the use of acidic media due to protonation effects. This agrees with the assertion obtained in this research work for Okobo coal, which postulates that coals of comparable geological composition but from different regions may reflect similar susceptibility to dissolution in acidic media.

3.3. Dissolution studies

The solvent medium exerts a substantial influence on the dissolving behaviour of Obajana limestone as shown in Table 3, indicating that acidic condition favours limestone breakdown with a percentage dissolution of 6.0531 ± 1.13. Higher acid concentrations give more protons to react with the carbonate ions in limestone, facilitating its breakdown. This result is in line with the laws of chemical kinetics. The dissolution process in hydrochloric acid medium indicates a notable weight loss (0.06077 ± 0.013 g) as compared to other media (0.05285 ± 0.009 g and 0.0044 ± 0.002 g for basic and neutral media respectively). This explains a higher reactivity of limestone with acidic solutions, which correlates with the chemical behaviour of calcium carbonate (CaCO3) reacting with hydrochloric acid to form calcium chloride (CaCl), water, and carbon dioxide.

The dissolution of Obajana limestone in sodium hydroxide was less pronounced (with a value of 5.2814 ± 0.93 %) as compared to hydrochloric acid. Limestone is less reactive in bases, as the dissolution process involves primarily the neutralization reaction forming calcium hydroxide, which is less soluble in water.

As observed in Figure 7 and Table 3, the dissolution of Obajana limestone in distilled water showed minimal weight loss of 0.0044 ± 0.002 g, indicating that the limestone is relatively stable in neutral pH environments. The findings from the dissolution studies of Obajana limestone agree with the general understanding of limestone chemistry. The higher dissolution rate in acid is as a result of the reaction of calcium carbonate with hydrochloric acid, which is a well-documented process [2].

Table 3: Dissolution of limestone in different media; acid and base (water as a control) as a function of time.

		Time (min)						
Media/Weight (g)		60	120	180	240	300	360	Mean ± SD
Acid	Wt_{Ai}	1.0021	1.0084	1.0007	1.0012	1.0071	1.0029	1.0037±0.003
	Wt_{Af}	0.9613	0.951	0.9435	0.9425	0.9337	0.9258	0.9429±0.013
	Wt_{Ad}	0.0408	0.0574	0.0572	0.0587	0.0734	0.0771	0.06077±0.013
% diss A		4.0714	5.6922	5.7159	5.8629	7.2883	7.6877	6.0531±1.13
Base	Wt_{Bi}	1.0001	1	1.0011	1.0008	1.0004	1.0015	1.00065±0.001
	Wt_{Bf}	0.956	0.9551	0.9526	0.9318	0.9441	0.9472	0.9478±0.009
	Wt_{Bd}	0.0441	0.0449	0.0485	0.069	0.0563	0.0543	0.05285±0.009
% diss B		4.4096	4.49	4.8447	6.8945	5.6277	5.4219	5.2814±0.93
Water	Wt_{Wi}	1.0002	1.0005	1.0021	1.0031	1.0005	1.0023	1.0015±0.001
	Wt_{Wf}	0.9981	0.9973	0.9972	0.9966	0.9938	0.9991	0.9970±0.002
	Wt_{Wd}	0.0021	0.0032	0.0049	0.0065	0.0067	0.0032	0.0044±0.002
% diss W		0.209	0.3198	0.4889	0.6479	0.6697	0.3192	0.4424±0.19

Key: Wt_A = Weight of Limestone in Acid, Wt_B = Weight of Limestone in Base,
Wt_W = Weight of Limestone in Water, Wt_{Xi} = Initial Weights,
Wt_{Xf} = Final Weights and Wt_{Xd} = Difference in Weight between Initial and Final,
% Diss X = Percentage Weight Dissolved, SD = Standard deviation.

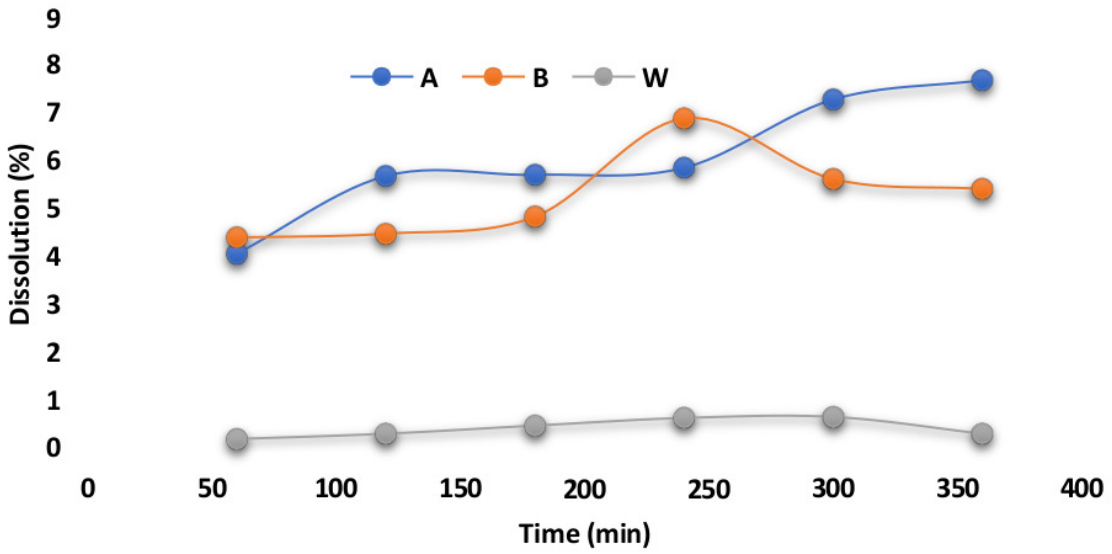


Figure 7: Dissolution profile of Obajana limestone in acid and base using water as control.

According to recent research on mineral dissolution kinetics, the solvent's chemical make-up and the experimental setup both affect how quickly different minerals dissolve [2, 9]. These results are consistent with these findings. Conversely, the lower dissolution rate in base is also expected, as calcium hydroxide formed during the reaction is less soluble, slowing down the dissolution process [20].

The stability of Obajana limestone in neutral water media attributes to its acceptability for construction and cement production, as also it suggests durability in less reactive environments [7]. These results are crucial for industries depending on limestone for manufacturing processes, as they create an in-depth knowledge into the behaviour of materials under different chemical conditions.

3.4. Dissolution kinetics modelling

3.4.1. Zero-order model

i. Acidic Medium: The model according to Table 4 (and Figures 8 and 9) showed a good fit at value at k_0 = 0.0001 g/min and R^2 = 0.8933. This is associated with a linear reaction between $CaCO_3$ and HCl, hence giving soluble calcium chloride ($CaCl_2$) [6]. This ought to agree with the general high reactivity of calcium carbonate with acids [16].

ii. Basic Medium: This medium fitted moderately with the lower R^2 of 0.3682 (Table 4). The reaction involves the formation of calcium hydroxide, which is of low solubility, hence limiting further dissolution, as reported by Magaji *et al*. [7].

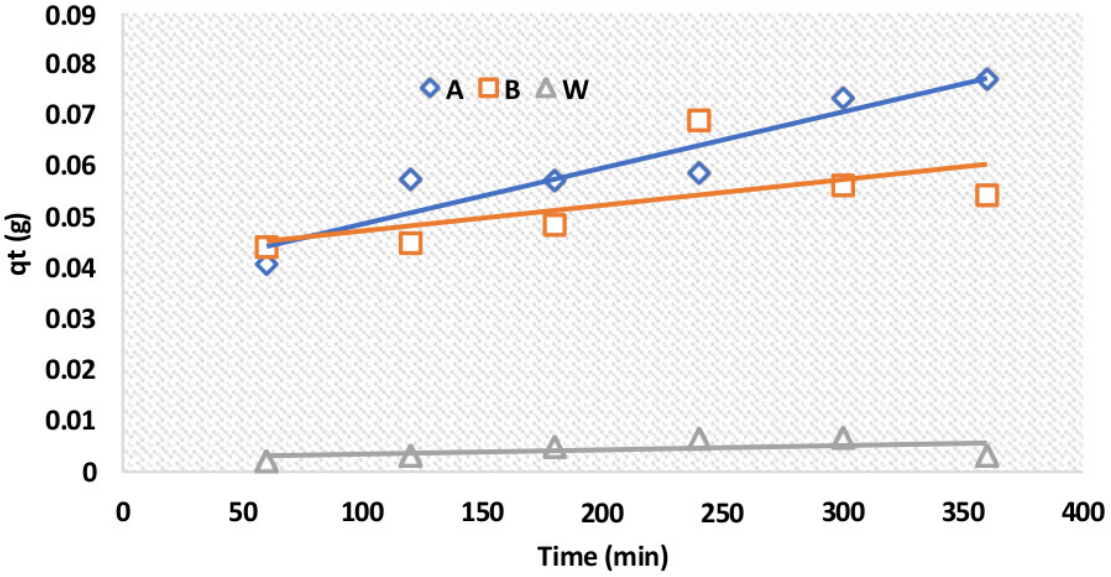


Figure 8: Zero order plots for dissolution of Obajana limestone in acid (A), base (B) and water (W).

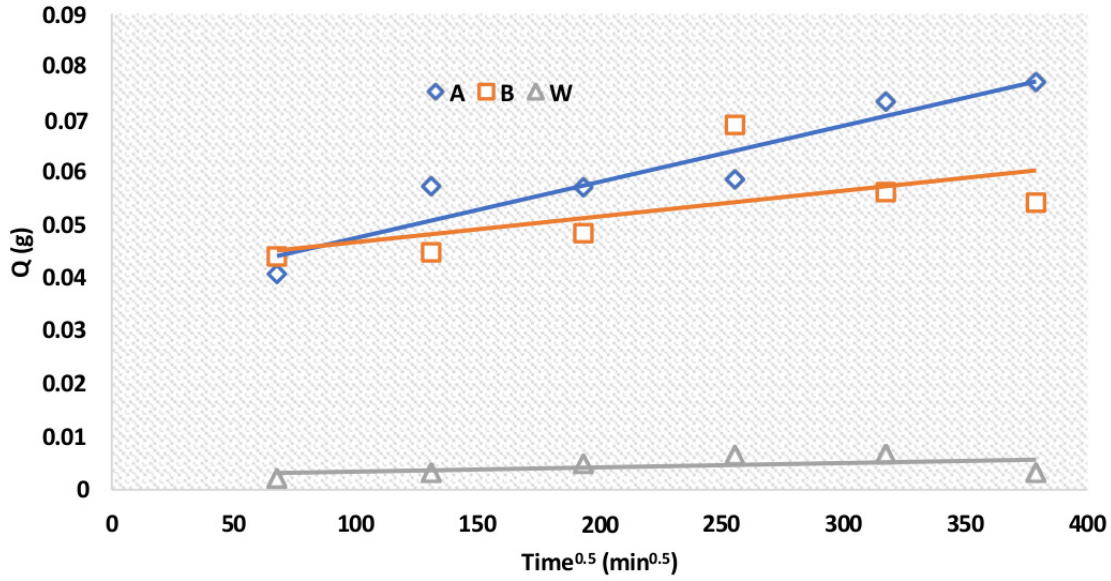


Figure 9: Higuchi plots dissolution kinetics of Obajana limestone dissolution kinetics in acid (A), base (B) and water (W).

Table 4: Experimental constants and parameters for the dissolution of Obajana limestone.

	Constants	Medium		
		A	B	W
Zero Order	R^2	0.8933	0.3682	0.2443
	k_o (g/min)	0.0001	5.0×10^{-5}	8.0×10^{-5}
Higuchi Model	R^2	0.8939	0.3698	0.2471
	K_H (g/min$^{0.5}$)	0.0001	5.0×10^{-5}	8.0×10^{-6}

Key: A=Acid, B=Base and W=Water

iii. Neutral Medium: The weakest fit was realized with zero-order, R^2 being 0.2443, indicating that limestone undergoes minimal dissolution without a significant change in pH, since it usually occurs in stable neutral water, according to Koech *et al.* [20].

In Obajana limestone, the best fit for the zero order was in acid at 0.8933 and g/min. The model is highly suitable for describing

the dissolution of limestone in acids; this is because the reaction between CaCO3 and HCl leads to the consistent formation of soluble calcium chloride CaCl and the release of CO gas. The strong fit indicates that the dissolution rate of limestone is constant provided there is sufficient acid present-a premise in conformity with observations by Gokhan, [16].

3.4.2. Higuchi model

1. Acidic Medium: On the other hand, the Higuchi model fitted well, manifested by R^2 = 0.8939 (Table 4), indicating diffusion-controlled dissolution favored in high proton concentration media [8].
2. Basic and Neutral Media: As shown in Table 4, the model fitted less in these media, with smaller values of R^2, which means that diffusive mechanisms driven by the process of dissolution are less effective, since it is a precipitation of calcium hydroxide, and it has low reactivity in neutral water [12, 21]

In comparison, both models showed good applicability for limestone dissolution, with the zero- order model describing a consistent dissolution rate, while the Higuchi model accounted for the diffusion process, especially in acidic conditions.

Such studies on limestones include those by Shih *et al*. [22] into Taiwan limestones, which also showed good fittings for the zero-order model in acid media; the values were mostly above 0.85. This consistency in trends of behaviour would therefore suggest that reactions between acids and limestones are the same in principle, given that they emanate from the dissolution of salts and release of gases. However, limestone samples from Brazil, studied by Oliveira *et al.* [5], reacted variably in basic media with compositional differences such as higher magnesium content. Relatively, the decrease in dissolution rate of Obajana limestone in basic media is due to higher calcium content favouring the formation of insoluble calcium hydroxide.

4. Conclusion

The zero-order model is suitable for an environment of linear dissolution, expressed by excess reactants or constant reaction conditions, as stated before in the case of an acid medium. The prominent fit of the zero-order model in acidic media for both minerals agree with global data and emphasizes the importance of mineral composition and environmental factors specific to Nigeria. Whereas in basic or neutral media, the development of precipitates and less solubility interferes with these conditions and reduces the applicability of the model. The relevance of the Higuchi model under acid conditions, especially for limestone, gives the view that there is a role of diffusion processes wherever the structure of the mineral permit permeation. The findings can be applicable in a number of industrial applications such as cement production, mineral extraction, and also contribute to effective environmental monitoring, remediation and management strategies. In order to build on the results of this study, further studies should be carried out on the effect of temperature and humidity to better simulate real-world conditions in dissolution rates of coal and limestone. Also, detailed mineralogical and chemical analyses of coal and limestone samples obtained from various regions in Nigeria should be done to provide explanations for the dissolution behaviour variation.

Data availability

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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