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Optimization and Kinetic Modeling of the Removal of Lead from Enugu Coal by Acid Leaching

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Authors' contributions

This work was carried out in collaboration among all authors. Author OSE designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors ACO and AMA managed the analyses of the study. Author AMA managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Removal of lead from Enugu coal with different acids as the leachant under different conditions such as leaching time, particle size, acid concentration, and leachant volume was investigated in this studies. The filtrate from each treatment was analyzed with Atomic Absorption X-ray Spectrometer (AAS) to determine the amount of lead leached. Nitric acid was found to be the best acid for the leaching of lead from Enugu coal. Kinetic studies carried out showed that the dissolution rate increased with: decreasing particle size, increase in stirring speed, acid concentration and leaching temperature. The experimental results revealed that the dissolution rate is a chemical reaction controlled via hydrogen ion concentration $[H^+]$, with reaction order of 0.9 and the reaction kinetics can be expressed as $1-(1-X)^{1/3} =2.566x10^{-4}(C_{HNO3})^{0.86} (dp)^{.992} (L/S)^{.44} (SS)^{.049} exp^{(53.49/RT)}$. A quadratic

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model was predicted and optimized using second order orthogonal design (Box-Benken) which resulted in Particle size of 40μm, reaction time of 8.5 hours, and HNO_3 concentration of 2mol/dm^3. The optimum conditions were validated at model desirability of 1. Experimental value of 96.39% with error of 0.530% was removed.

Keywords: Optimization; box-benken; Enugu coal; trace elements; lead.

1. INTRODUCTION

Coal is formed in seams of varying thickness, which are imbedded between the rock formations of three out of the main five periods in the earth's geological history. It is a combustible solid and is a common source of energy in many homes and industries [1]. The availability and relative important of fossil fuels has changed with the passage of time. Primitive man was satisfied with the burning of wood for heating and cooking but coal originally from surface and subsequently from underground mining, replaced wood as the dominant fuel [2]. The warmth-giving properties of coal were most probably discovered by early fire-making and tool-using men in various parts of the world by the so-called cavemen [3].

Highly toxic elements (e.g. arsenic, mercury, lead and selenium), are present in coals though generally in very low concentrations [4,5]. However, hazardous elements present in very low amounts adversely impact the environments in a matter of scales. Annually, millions of tons of coal are mined and utilized potentially liberating large amounts of various hazardous elements. For example, a coal fired power plant with no pollution controls in place theoretically would produce 10 tons of lead for each million tons of coal burned containing 10 ppm lead. However, more pollution control measures provide control against the release of large amounts of hazardous trace elements to the environment. Due to the potential effects of pollutants from coal fired power plants, environmental protection agency (EPA) are currently investigating whether further regulation of trace element emission are necessary [6].

Leaching of coal samples before combustion or before use for power plant operations will surely remove most of the trace elements in that coal thereby minimizing its environmental problems. Removal of materials by dissolving them away from solids is called leaching. Enugu coal has been found to contain greater quantity of lead (trace element) when compared with other trace elements according to Onwu [7]. Therefore, this research is aimed at investigating the removal of a trace element (Lead) from Enugu coal by the action of mineral acids and thereafter optimizes the process parameters using response surface methodology.

2. MATERIALS AND METHODS

2.1 Sourcing of Raw Materials

Raw materials used in this investigation included: coal, mineral acids and distilled water. Sample of coal was sourced from Onyeama mine Enugu through Enugu coal co-operation while the mineral acid and distilled water was purchased from the local market in Enugu State, Nigeria.

2.2 Coal Sample Preparation

Sample of coal obtained was thoroughly washed with distilled to remove debris and sand and dried under the sun for 5hours. Dried coal sample was crushed and grounded in a pestle and mortar and screened through 75μM sieves using a sieve shaker. The definite sized coal sample was further dried in a vacuum oven at 110°C for one hour and cooled in desiccators. The original coal sample was digested using a mixture of hot concentrated nitric (800ml/l) and perchloric acids (200ml/l) and analyzed for trace elements Pb, Cd, Cr, As and Hg using Atomic Absorption spectrometer (AAS).

2.3 Characterization of Coal Samples

Moisture content, Ash content, volatile matter and fixed carbon were analyzed by loss on ignition using the standard method ASTM D2974 [8]. An FS 240 variant Atomic Absorption Spectrophotometer (AAS) using Nitrous oxide oxidant gas, Acetylene gas, Air oxidant gas, distilled water, and conical flask were used for the analysis of lead. The micrograph of the original and residual coal sample was determined using scanning electron microscope (SEM).

2.4 Extraction of Trace Metal (Leaching of Lead)

5 grams of pulverized coal sample was measured into a 100ml beaker of different volumes of acids of different concentrations. The mixtures were shaken vigorously and placed in a water bath set at 65°C for 8 hours with intermittent stirring. The mixtures were filtered using filter paper No. 1. The filtrate was then taken to laboratory for analysis while the residue was washed thoroughly with several amount of distilled water to remove all traces of acid. The washed coal residue was placed in the oven set at 50°C to dry and weighed until constant weight was obtained. The dried coal residues were cooled in desiccator and later taken to laboratory for further analysis. The whole experimental procedure was repeated to determine the effect of parameter such as contact time, particle size, acid concentrations, and volume of leachant.

2.5 Experimental Design for the Screening of the Process Variables

The experiment was designed as shown in Table 1 to determine if there is any significant effect of five different acid types under the different process conditions (process duration, particle size of coal samples, acid concentration, and volume of leactant) on the removal of lead from Enugu coal. Since, there are five factors, having also five levels each, Graeco-Latin square analyses of variance were used.

Hence,

X_1 = particle size (P_1, P_2, P_3, P_4, P_5)
X_2 = process duration (T_1, T_2, T_3, T_4, T_5)
X_3 = Acid type (A, B, C, D & E)
X_4 = Acid concentration (N, H, S, J, K
X_5 = Volume of leachant (α, β, λ, θ, δ).

With X_1 = 75, 63, 40, 30 and 23µm, X_2= 8, 16, 24, 32 and 40hours, X_3= HCl, H_2SO_4, HNO_3, HF and H_3PO_4, X_4= 0.5, 1.0, 1.5, 2.0 and 2.5M, while X_5= 20, 40, 60, 80 and 100 mls.

2.6 Experimental Design for the Optimization of the Process Variables

Design Expert software (version 9 trial version) was used in this study to design the experiment and to optimize the reaction conditions. The experimental design employed in this work was Orthogonal Second-order Design (Box-Benkhen Design). Particle size, leaching time and acid concentration were selected as independent factors for the optimization study. The response chosen was the Percentage of lead leached. Five replications of centre points were used in order to predict a good estimation of errors and experiments were performed in a randomized order. The actual and coded levels of each factor are shown in Table 2. The coded values are designated by −1 (minimum), 0 (centre), +1 (maximum).

Box-Benkhen design for three factors follows a quadratic model of the form:

$$Y = b_o + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \quad (1)$$

where:

b_0 is the real intercept value of the regression model

$b_1, b_2,$ and b_3 are real regression coefficients for single factors respectively.

b_{12}, b_{13} and b_{23}, are real regression coefficients for interacting factors respectively.

b_{11}, b_{22} and b_{33} are real regression coefficients for self-interacting factors respectively.

ε is called random error or residual which is the amount of variation in the response (*Y*) not accounted for by the quadratic relationship.

Y is the response, and X_1, X_2, and X_3 are independent factors – Particle size, leaching time, and strength of acid respectively.

2.7 Kinetics of Leaching Process

The leaching kinetics experiments were carried out in a round bottom flask fixed to hot magnetic stirrer. A known mass of the ground coal sample was dispersed in the leaching liquid with a known liquid-solid weight ratio and placed on the hot magnetic stirrer. The reaction started with a particular leaching temperature and stirred at constant speed of 500rpm for a known leaching time. Then micro pipette was used to collect 1ml of the suspension and properly diluted to the 100 ml mark with distilled water and filtered using filter paper. The filtrate was taken to the Atomic Adsorption Spectra machine to determine the concentration of metal (lead) present.

Table 1. Graeco-latin square plan of five factors and five levels

X_1 \ X_2	T_1	T_2	T_3	T_4	T_5
P_1	Sample 1 B θ H	Sample 2 C λ N	Sample 3 A δ S	Sample 4 E α J	Sample 5 D β K
P_2	Sample 6 A λ J	Sample 7 B α S	Sample 8 D θ K	Sample 9 C β N	Sample 10 E λ H
P_3	Sample 11 C δ S	Sample 12 E θ J	Sample 13 B β H	Sample 14 D λ K	Sample 15 A λ N
P_4	Sample 16 D α N	Sample 17 A β K	Sample 18 E λ J	Sample 19 B δ H	Sample 20 C θ S
P_5	Sample 21 E β K	Sample 22 D δ H	Sample 23 C α N	Sample 24 A θ S	Sample 25 B λ J

Thus there are a total of 25 experiments using different combinations of the process variables

Table 2. Independent variable with real values

Parameter	Low level	Null point	High Level
Particle Size(μm) **A**	35 (-1.000)	40 (0.000)	45 (+1.000)
leaching Time (hours) **B**	7.5 (-1.000)	8 (0.000)	8.5(+1.000)
Acid conc (M) **C**	1.0 (-1.000)	1.5 (0.000)	2.0 (+1.000)

Table 3. Box-behnken design matrix represented in coded values of factors for the leaching of lead from Enugu coal

Std	Run	Factor 1 A: Particle size (μm)	Factor 2 B:Leaching Time (hours)	Factor 3 C:Acid Concentration (M)
13	1	0.000	0.000	0.000
10	2	0.000	1.000	-1.000
16	3	0.000	0.000	0.000
7	4	-1.000	0.000	1.000
5	5	-1.000	0.000	-1.000
17	6	0.000	0.000	0.000
3	7	-1.000	1.000	0.000
6	8	1.000	0.000	-1.000
8	9	1.000	0.000	1.000
4	10	1.000	1.000	0.000
12	11	0.000	1.000	1.000
9	12	0.000	-1.000	-1.000
14	13	0.000	0.000	0.000
11	14	0.000	-1.000	1.000
2	15	1.000	-1.000	0.000
1	16	-1.000	-1.000	0.000
15	17	0.000	0.000	0.000

In order to establish the kinetic parameters and rate-controlling step for the leaching of lead from 'Enugu Coal' in nitric acid solution, the experimental data were fitted to the kinetic models. Such plots are quite extensively used in kinetic studies [9]. The kinetic relationships are expressed in terms of the fraction of reacted particle X, with time. Three established models i.e. chemical reaction controlled process, liquid film diffusion controlled process, and product layer diffusion controlled process were considered for initial selection of the reaction mechanism. The equations for these models as proposed by Sultana, et al. [10] are as follows:

Chemical reaction controlled process

$$k_c t = 1 - (1-X)^{\frac{1}{3}} \quad (2)$$

Liquid film diffusion controlled process:

$$k_f t = 1 - (1-X)^{\frac{2}{3}} \quad (3)$$

Product layer diffusion controlled process;

$$k_p t = (1 - \frac{2X}{3}) - (1-X)^{\frac{2}{3}} \quad (4)$$

where,

X = fraction of reacted particles

k_c, k_f , k_p = rate constants for chemical reaction controlled, liquid film diffusion controlled and product layer diffusion controlled respectively.

In addition to the heterogeneous models tested, pseudo-homogeneous first models were also tested. In the pseudo-homogeneous model, the rate equation is written as:

$-ln\ (1 - X) = K_i t$ (First-order pseudo homogeneous model) (5)

$-ln\ (1 - X) = Kat^m$ (Avremi model) (6)

The models were tested at temperatures of 30°C, 40°C, 50°C, and 60°C and 70°C.

Activation energy for the leaching was obtained using Arrhenius equation.

$$K = k_0 e^{\frac{-E}{RT}} \quad (7)$$

Equation 7 in linear form gave Equation 8.

$$\ln k = \ln k_0 \frac{E}{R}\frac{1}{T} \quad (8)$$

where k = first order rate constant obtained from leaching kinetic mechanism, k_0 = pre exponential factor, E = activation energy, R = gas constant (8.314kJ/molK), T = temperature.

The plot of $\ln k$ verses $\frac{1}{T}$ gives slope from which the activation energy is calculated while the intercept gives $\ln k_0$.

3. RESULTS AND DISCUSSION

The results of the Proximate Analysis conducted on the coal sample of particle size 75μm are presented as shown in Table 4. The total moisture content, volatile matter content, ash content and fixed carbon was found to be 10.10%, 25.4%, 7.6% and 56.9% respectively and these values were in accord with the results reported by Onwu [7], Ann [5]. From Table 4, it can be concluded that the coal sample is sub-bituminous coal according to American society for testing and materials (ASTM) classification of coal.

Table 4. Proximate analysis of original coal sample

Properties	Weight (%)
Surface moisture	0.70
Inherent moisture	9.40
Total moisture content	10.10
Volatile matter	25.40
Ash content	7.60
Fixed carbon	56.90

3.1 SEM Observations of the Untreated and Treated Coal Samples

SEM micrographs of the original coal sample and leached sample are provided in Fig 1 and 2. Fig 1 represents the SEM image of the original coal sample at 30μm. It can be observed from the Figure that a bulk of microstructure which in turn is composed of a homogeneously distributed network comprised of small filamentous and fistulous crystallites showing the presence of minerals. In the matrix, Luminous and non-luminous features can be seen. These features indicate the presence of minerals distributed in the organic matrix and as surface coverage. Some features such as fissures, cleats, cracks and veins can also be seen. The bright luminosity indicates the presence of lithophytes like magnesium, aluminum, silicon, calcium, titanium etc, and sidrophile, like iron and the dark luminosity indicates the presence of chalcophiles like lead, chromium, cadmium, arsenic, mercury, copper, zinc etc. etched pits, layers, some islands and hills and valleys can be seen randomly distributed throughout the micrograph. These might be resulted from the calculations of dolomite like $CaMg(C0_3)_2$ and calcites like $CaCO_3$, or their assemblage due to the thermal shock during metamorphism. Some discrete and coherent crystals (framboids, and enthedral) of irregular shapes represent the presence of iron. Veins corresponding to iron oxides can also be seen. It is inferred that Enugu coal under study contains large proportions of silica, calcite, and dolomite as well as some proportions of elements such as aluminum, iron, and potassium and other trace metals such as lead, chromium, cadmium, arsenic, mercury, copper, etc that proved to be in agreement with other the report by Ohiki et al. [11].

In order to remove the minerals and enrich the coal in usable carbon, chemical leaching was performed with mineral acid (HNO_3) at a combination of factors such as, time of leaching, acid concentrations, particle sizes, volume of leachant.

From Fig. 2, it can be seen that the porosity has been increased and provides strong evidence that significant amounts of inorganic elements are being removed. However the surface coverage is still bright and luminous indicating the presence of mineral phases. It can also be seen that in the micrograph, the leachant did little harm to the surface and the surface is as intact as to the virgin coal as shown in Fig. 1. The reason might be some of the dolomite mineral phases have gotten dissolved at the selected pH and have re-deposited on the surface instead of their removal. Furthermore, it can be seen that the HNO_3 caused morphological changes in the particles and did enormous harm to the surface by leaching some of the inorganic elements. However the acid used with the combination of factors for the experiment seems to be more effective in leaching out elements from the coal under study. Similar change in morphology of coal by action of mineral acid was reported by Giampaolo et al. [12]

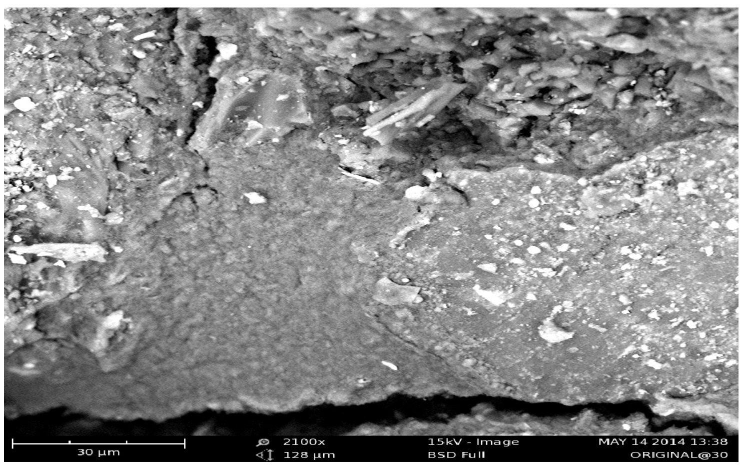

Fig. 1. SEM micrograph for original coal at 30 µm

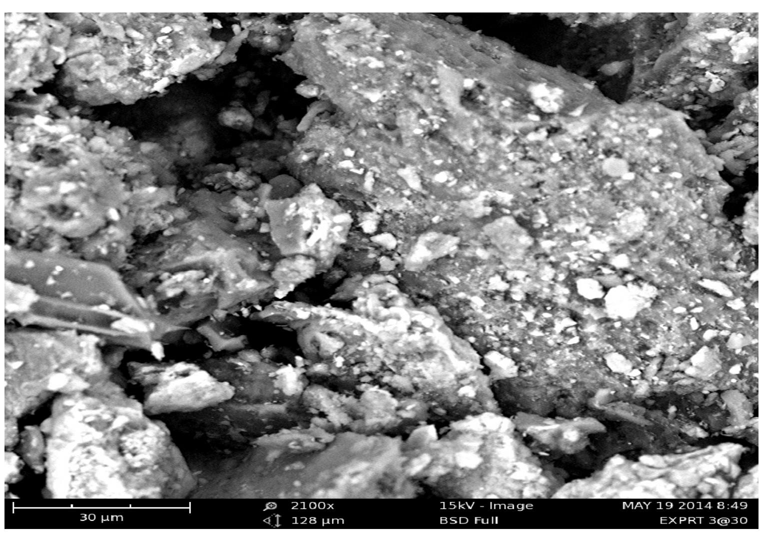

Fig. 2. SEM micrograph of coal treated with, HNO_3 at 30 µm

3.2 AAS Analysis Results

The results of the atomic absorption X-ray spectrophotometry (AAS) of the filtrate for mineral analysis of the digested raw coal and treated samples were given in Tables 5 and 6. The trace metals analyzed in the raw coal include lead, chromium, cadmium, arsenic and mercury. This is based on the fact that these five elements are among the metals mentioned by prior researchers including [1,13,14] that constitute environmental problems. From Table 5, it was observed that Enugu coal contained more of lead (Pb). The original coal contained very high concentration of lead (10.4ppm) as shown in Table 5. The best condition for the removal of lead as shown in Table 6 was recorded during experiment for sample 11 (with C = HNO_3, S= 1.5M, δ = 100mls, P = 40μm and T= 8 hours as shown in Table 1) which resulted in the leaching out of 8.40 ppm of lead from initial concentration of 10.4 ppm present in original coal sample as shown in Table 6. These results are in agreement with the report by Poon et al. [6], that mineral acids are good leachants for trace elements removal from coal samples. Hence one can conclude that the best acid for the leaching of lead is HNO_3. Similar results were reported also by Mohammad et al. [13].

Concentration of lead as shown in Table 6 was subjected to statistical analysis and the analysis of variance (ANOVA) was used as shown in Table 7 to test the significant effects of some parameters such as acid type, acid concentration, particle size, volume of leachant and leaching time on the leaching of lead from Enugu coal.

At 0.01 level of significance from Fischer troph statistical table and $V_1 = V_2 = V_3 = V_4 = V_5 = 4$ and Vres = 8, the critical F-value (0.01, 4, 8) = 7.01.

Table 5. AAS analysis of original coal samples

Sample	Amount (ppm)				
	Pb	Cr	Cd	As	Hg
Raw coal	10.4	0.20	0.24	0.51	0.10

Table 6. Fraction of lead in the residual coal

Coal samples with experimental conditions	Amount of lead removed after leaching (ppm)
Sample 1	0.80
Sample 2	1.80
Sample 3	1.20
Sample 4	4.10
Sample 5	3.70
Sample 6	0.90
Sample 7	2.20
Sample 8	0.30
Sample 9	0.20
Sample 10	1.10
Sample 11	8.40
Sample 12	0.50
Sample 13	0.40
Sample 14	1.70
Sample 15	1.40
Sample 16	0.30
Sample 17	0.40
Sample 18	0.50
Sample 19	0.30
Sample 20	0.40
Sample 21	0.50
Sample 22	0.40
Sample 23	0.30
Sample 24	0.30
Sample 25	0.40

Table 7. Summary of ANOVA result for leaching of trace metal (Lead) from Enugu Coal

Source of variance	Sum of squares	No of degree of freedom	Estimate of variance	Variance ratios
X_1 = particle Size	25.83	4	6.46	38.92
X_2 = leaching time	18.21	4	4.55	27.41
X_3 = acid type	6.68	4	1.67	10.06
X_4 = Leachant Volume	2.492	4	0.623	3.75
X_5 = Acid Con.	10.22	4	2.56	15.42
Residual	1.33	8	0.166	-
Total	77.05	28	19.11	114.10

Since F_1 > Ftable, F_2 > Ftable, F_3 > Ftable, F_4 < Ftable and F_5 > Ftable, then x_1, x_2, x_3, and x_5 are all significance while x_4 is insignificant. This means that, the leaching of trace metal (lead) depend on the particle size, leaching time (duration), acid type, reachant volume, and acid concentration.

However, at 0.05 level of significance and $V_1 = V_2 = V_3 = V_4 = V_5 = 4, 8 = 3.84$.

Since F_1 > Ftable F_2 > Ftable, F_3 > Ftable, F_4<Ftable and F_5 > Ftable, then the x_1, x_2, x_3, and x_5 are all significant while x_4 is insignificant. This is also means that the leaching of trace metal (lead) from Enugu coal depends on the particle size, leaching time, acid type, and acid concentration.

With these results, it can be concluded that at any level of significance, the leaching of trace metals (lead) depends on the coal particle size, duration of leaching, acid type, and acid concentration and also, any volume of leachant (solid/liquid ratio) would have effect in removal of lead from Enugu coal. Hence, the factors in row 4 column 2 of Table1 which lead to the reduction in concentration of lead from 10.4ppm to 0.2ppm during experiment for sample 11 was selected and optimized.

The Model F-value of 63.99 implies the model is significant. Values of "Prob> F" less than 0.0500 indicate model terms are significant. In this case B, C, A^2, B^2, C^2 are significant model terms.

Table 8. Box benken design with response for the leaching of lead with conc HNO_3

Parameter	Low Level (-1.000)	Null Point (0.000)	High Level (+1.000)
A: Particle size(μm)	35	40	45
B: Leaching Time (hours)	7.5	8	8.5
C: Acid Conc (M)	1.0	1.5	2.0

		Factor 1	Factor 2	Factor 3	Response 1
Std	**Run**	**A:Particle size (μm)**	**B:Leaching Time (hours)**	**C:Acid Conc (M)**	**Percentage removed**
13	1	0.000	0.000	0.000	96.38
10	2	0.000	1.000	-1.000	93.12
16	3	0.000	0.000	0.000	96.39
7	4	-1.000	0.000	1.000	91.09
5	5	-1.000	0.000	-1.000	92.28
17	6	0.000	0.000	0.000	96.39
3	7	-1.000	1.000	0.000	93.98
6	8	1.000	0.000	-1.000	92.33
8	9	1.000	0.000	1.000	91.18
4	10	1.000	1.000	0.000	94.18
12	11	0.000	1.000	1.000	92.46
9	12	0.000	-1.000	-1.000	91.98
14	13	0.000	0.000	0.000	96.39
11	14	0.000	-1.000	1.000	90.06
2	15	1.000	-1.000	0.000	91.01
1	16	-1.000	-1.000	0.000	90.78
15	17	0.000	0.000	0.000	96.39

The "Pred R-Squared" of 0.8079 is in reasonable agreement with the "Adj R-Squared" of 0.9726; i.e. the difference is less than 0.2. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. "Adeq Precision" ratio of 22.732 indicates an adequate signal. This model can also be used to navigate the design space.

Final regression equation in terms of coded factors for the leaching of lead:

$$\text{Amount of lead } (Y) = +96.39 + 0.071 * A + 1.24*B - 0.62*C - 7.5E\text{-}003*AB + 0.010*AC + 0.31*BC - 2.04*A^2 - 1.86*B^2 - 2.63*C^2 \quad (9)$$

Table 9. Analysis of variance [partial sum of squares - Type III] for the leaching of lead

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remark
Model	83.82	9	9.31	63.99	< 0.0001	Significant
A-Particle size	*0.041*	*1*	*0.041*	*0.28*	*0.6137*	
B-Leaching Time	*12.28*	*1*	*12.28*	*84.34*	*< 0.0001*	
C-Acid Conc	*3.03*	*1*	*3.03*	*20.79*	*0.0026*	
AB	*2.250E-004*	*1*	*2.250E-004*	*1.546E-003*	*0.9697*	
AC	*4.000E-004*	*1*	*4.000E-004*	*2.748E-003*	*0.9597*	
BC	*0.40*	*1*	*0.40*	*2.73*	*0.1427*	
A^2	*17.57*	*1*	*17.57*	*120.71*	*< 0.0001*	
B^2	*14.53*	*1*	*14.53*	*99.83*	*< 0.0001*	
C^2	*29.02*	*1*	*29.02*	*199.36*	*< 0.0001*	
Residual	1.02	7	0.15			
Lack of Fit	*1.02*	*3*	*0.34*	*16980.42*	*< 0.0001*	
Pure Error	*8.000E-005*	*4*	*2.000E-005*			
Cor Total	84.84	16				

Std. Dev.	0.38	R-Squared	0.9880
Mean	93.32	Adj R-Squared	0.9726
C.V. %	0.41	Pred R-Squared	0.8079
PRESS	16.30	Adeq Precision	22.732

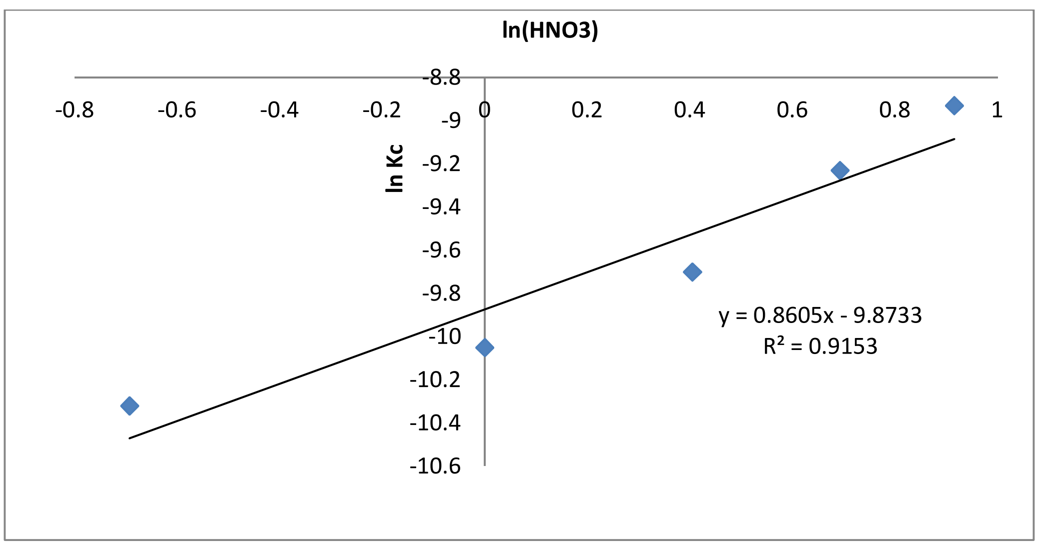

Fig. 3. Plot of natural logarithm of reaction rate constant versus natural logarithm of acid concentration

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels are specified in the original units for each factor. This equation was not used to determine the relative impact of each factor because the coefficients were scaled to accommodate the units of each factor and the intercept was not at the center of the design space.

3.3 Kinetics of Leaching of Enugu Coal

The reaction kinetics data for the leaching of lead (pb) from Enugu Coal using nitric acid solutions were analyzed both graphically and statistically using the shrinking core models, the first – order homogeneous model, and the Avremi model. The result showed that the experimental data did not fit into the first-order homogeneous and Avremi models when plotted in a graph. A straight lines passing through the origin were not obtained, low regression coefficient values were also calculated as shown in Table 11. When the data were analyzed using shrinking core models, it was observed that the data fitted very well to the chemical reaction controlled model for the different process parameters such as, acid concentration, particle size, temperature, liquid-to-solid ratio, and the stirring speed respectively. Therefore, the dissolution process was found to follow the shrinking core model and can be represented as follow:

$$1-(1-x)^{1/3} = k_c t \qquad (10)$$

The plot of the Arrhenius equation is shown in Fig 3 and the slope of the Figure was used to calculate the activation energy to be 47.15kj/mol. This value is within the range value of the dissolution kinetics of coal [15].

The effect of the process parameters, acid concentration, particle size, temperature, liquid/solid ratio, and stirring speed on the dissolution kinetics of Enugu Coal in Nitric acid, was investigated by postulating a semi-empirical model as follows

$$1-(1-x)1/3 = k_o C^{a}_{(HN03)} (dp)^{b} (L/S)^{c} (SS)^{d} \exp(-Ea/RT) \qquad (11)$$

The constants a ,b ,c, and d were calculated from the plots of the relationship between the natural logarithm of the calculated apparent rate constant and the natural logarithm of the process parameters, acid concentration, particle size, liquid/solid ratio, and stirring speed as shown in Figs. 3, 4, 5 and 6 respectively. While k_o and Ea were calculated from the Arrhenius plot. The value of a, b, c, d, K_o and E_a calculated are, 0.86, 0.992, 0.44, 0.492, 47.15, and 2.566 x 10^{-4} respectively. Putting the values into equation 12, gives

$$1-(1-x)^{1/3} = 2.566 \times 10^{-4} C^{0.86}_{HN03} (dp)^{.992} (L/S)^{.44} (SS)^{0.49} \exp\left(\frac{53.49}{RT}\right) \qquad (12)$$

A conclusion can be drawn that the dissolution of lead (pb) from Enugu Coal using nitric acid can be described by equation 12.

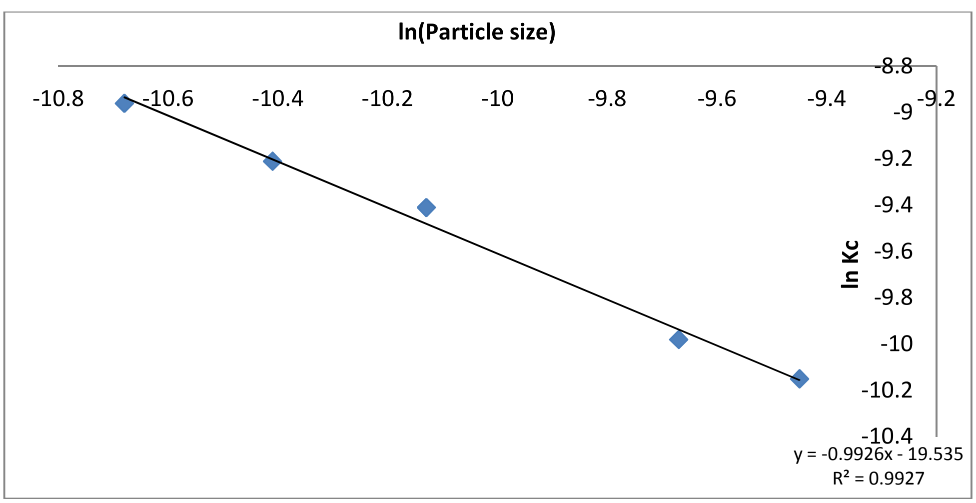

Fig. 4. Plot of natural logarithm of reaction rate constant versus natural logarithm of particle size

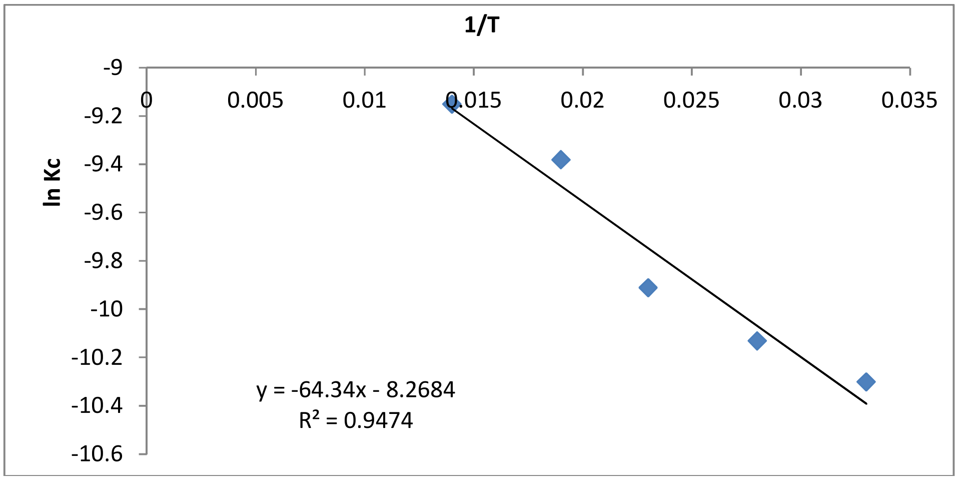

Fig. 5. Natural logarithm of reaction rate constant versus reciprocal of temperature

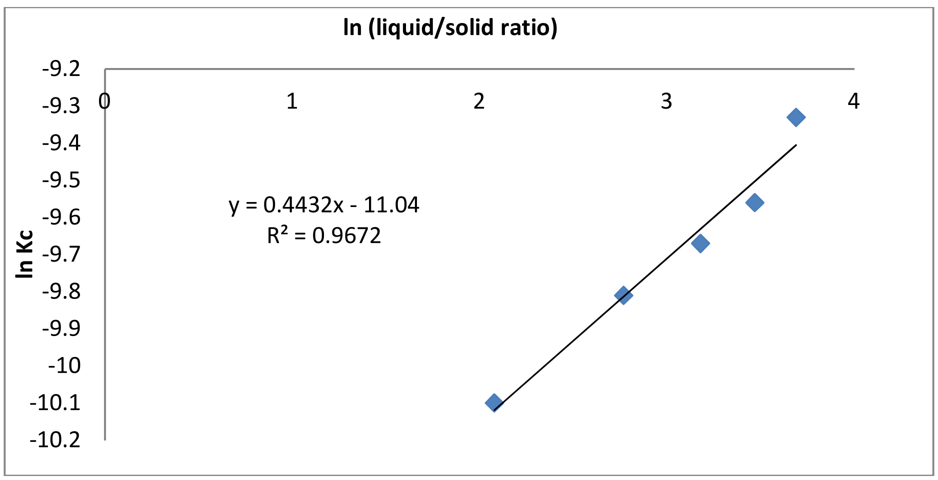

Fig. 6. Natural logarithm of reaction rate versus natural logarithm of liquid/solid ratio

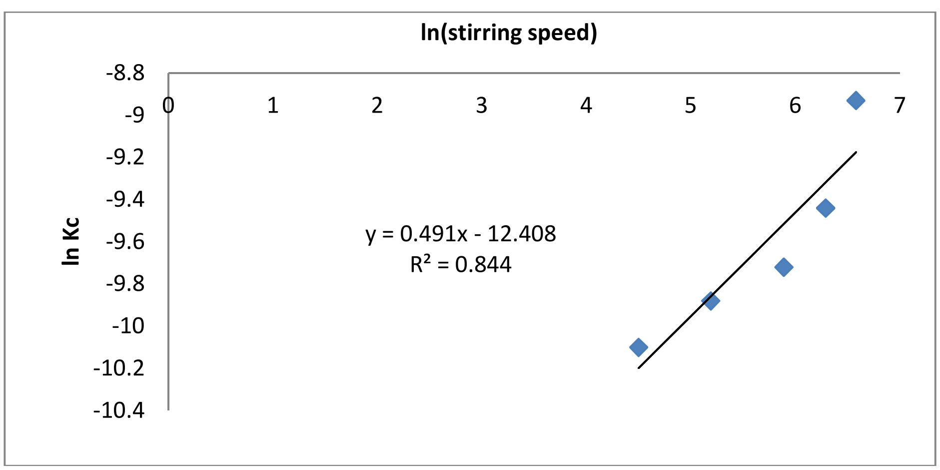

Fig. 7. Plot of natural logarithm of the reaction rate constant versus the natural logarithm of the stirring speed

Table 10. Numerical optimization of process parameters for the Leaching of lead from Enugu Coal

Number	Particle size*	Leaching Time*	Acid conc*	Desirability	Remark
1	40.0μm	8.50 hours.	2.0M	1.000	Selected

Table 11. Kinetic models with calculated kinetics parameters for the removal of lead from Enugu coal using Nitric acid as leachant

Process	Model									
Parameter	**Film diffusion**		**Product layer diffusion**		**Chemical reaction**		**Pseudo-first-order**		**Avremi**	
Acid conc. (mol/dm^3)	**Kf $X10^4$**	**R^2**	**Kp$X10^4$**	**R^2**	**Kc$X10^4$**	**R^2**	**Ki $X10^4$**	**R^2**	**Ka $X10^4$**	**R^2**
0.5	0.917	0.994	0.0715	0.988	0.330	0.998	3.20	0.995	1.2	.996
1.0	9.60	0.979	0.130	0.953	0.431	0.996	1.38	0.981	1.7	.987
1.5	1.54	0.980	0.277	0.892	0.613	0.989	1.998	0.966	1.98	.968
2.0	2.15	0.859	0.701	0.745	0.985	0.940	3.47	0.819	2.2	.898
2.5	2.60	0.996	1.22	0.911	1.33	0.999	4.99	0.957	2.7	.958
Particle size										
75μm	1.063	0.967	0.0988	0.994	0.390	0.9992	3.20	0.913	.98	.943
63μm	1.21	0.942	0.176	0.997	0.465	0.998	1.28	0.962	1.1	.971
40μm	1.13	0.962	0.269	0.984	0.822	0.984	1.998	0.965	1.3	.973
30μm	2.13	0.979	0.788	0.966	0.996	0.997	3.47	0.643	1.5	.849
23μm	2.46	0.974	1.20	0.987	1.28	0.991	4.99	0.993	1.63	.992
Temperature (°C)										
30	0.942	0.968	0.0722	0.838	0.335	0.981	1.05	0.988	.76	.989
40	1.04	0.965	0.152	0.892	0.398	0.975	1.28	0.954	.86	.962
50	1.17	0.978	0.310	0.896	0.498	0.982	1.70	0.978	.98	.980
60	2.13	0.967	0.676	0.949	0.848	0.981	3.04	0.968	1.05	.971
70	2.02	0.979	1.02	0.963	1.06	0.989	3.98	0.972	1.21	.981
Liquid/solid ratio (ml/g)										
20/2.5	0.958	0.971	0.0817	0.962	0.384	0.979	1.2	0.973	.66 .74	.975
40/2.5	1.43	0.984	0.204	0.956	0.547	0.989	1.71	0.985	.87	.986
60/2.5	1.56	0.988	0.325	0.932	0.633	0.989	2.13	0.978	.987	.981
80/2.5	1.58	0.966	0.476	0.871	0.702	0.979	2.43	0.946	1.10	.956
100/2.5	7.33	0.986	0.831	0.999	0.883	0.9996	3.31	0.999		.984
Stirring speed (rpm)										
90	1.13	0.974	0.085	0.925	0.412	0.975	1.303	0.965	56	.969
180	1.33	0.980	0.209	0.929	0.514	0.987	1.66	0.965	.65	.971
360	1.42	0.990	0.332	0.965	0.603	0.9996	2.03	0.993	.77	.980
540	1.73	0.994	0.593	0.942	0.794	0.995	2.76	0.969	.87	.979
720	2.32	0.989	1.43	0.916	1.33	0.994	5.325	0.941	.94	.961

4. CONCLUSION

The leaching of trace metals were found to be dependent on the leaching conditions such as acid concentration, particle size of coal sample, leaching time (contact time), volume of leachant (solid/liquid ratio). It was established that the leaching of any trace metal from Enugu coal depend on the acid type, acid concentration, particle size of coal, leaching time and solid/liquid ratio. The result from AAS showed that the maximum value of lead leached was achieved with 0.5Mol of $HN0_3$ at 32hrs, 63μm and 40ml volume. The SEM image of the residual coal from the acids treatment revealed that this leachants had caused morphological changes in the sample and did enormous change to the surface by leaching many of the inorganic elements.

HNO_3 was found to be a better leachant for leaching minerals from coal, but different metals required different acid with different concentration, leaching time, volume of leachant, and the particle size. It can also be concluded that the dissolution rate increases with increase in acid concentration.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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