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Effects of Particle Size on Bioleaching of Iron from Silica Sand Fitted to Shrinking Core and Mixed Kinetic Models

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Abstract: **The effects of particle size on the bioleaching of iron from naturally occurring silica sand with *Aspergillus niger* have been studied. Bioleaching tests were carried out with five different particle size fractions of silica sand, +120-212µm, +212-300µm, +300-425µm, +425-650µm and +650-1000µm at room temperature of 30±2^{0}C. It was only with the particle size, +120-212µm was the iron content of sand reduced to 0.11% which met the British standard for production of F and G grades of glass products. The experimental data were correlated with the chemical reaction model and ash layer diffusion equations of the Shrinking core model and a mixed kinetic model, which is a combination of both. The chemical reaction equation failed to represent the data; ash layer diffusion accounted for bioleaching of iron between day 21 to day 30. The mixed model largely represented the bioleaching process for the 30 days.**

Keywords: **Silica Sand, *Aspergillus niger*, Bioleaching, Iron, Particle Size, Kinetic Models, Shrinking core.**

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1. INTRODUCTION

The glass industry primarily depends on silica sand as raw material. Silica sand is a primary component of all types of standard and specialty glass. It provides the essential Silicon Oxide (SiO_2) component of glass formulation and its chemical purity is the primary determinant of colour, clarity and strength (NISA, 2011). Naturally occurring Silica sand contains iron and clay materials which coat silicate grains or are impregnated in silica matrix. Silica sand used for glass production has permissible limits of impurities especially iron oxide depending on the grades of glass to be produced.

Discrete particles of iron are removed by several processes, which include gravity settling and floatation. However, stains on the surface and in the matrix of the silica sand may require beneficiation, heat treatment and acid wash to remove them. These methods are energy intensive and not ecofriendly. Even the chemicals that are used are hazardous and expensive. Several researchers have demonstrated that various microorganisms participate in metal extraction, metal concentration, metal detoxification and desulphurization processes (Styriakiova *et al*,2007). *Aspergillus niger* has been used in the bioleaching of metals, particularly iron from silica sand (Mandal and Banerjee, 2003; Xu and Ting, 2003; Ndukwe and Chikwendu, 2010; Bayat *et al.*, 2011). These studies have shown *Aspergillus niger* for bioleaching of iron from silica sand as a viable option for replacement of the conventional heat/chemical treatment which is not only expensive but also hazardous.

Mustafa *et al* (2011) have shown that contact time, pH, incubation temperature and carbon source play vital role in the bioleaching of iron from silica sand. Their study agreed with an earlier study by Ndukwe and Chikwendu (2010) which identified pH and contact time as part of the key parameters which influence the extent of bioleaching of iron from silica sand.

Bioleaching belongs to a class of industrial operations in which surface properties of solid particles influence the reaction kinetics (Sadowski and Szubert, 2010). Several authors have used expressions similar to the unreacted shrinking core model to describe the process of bioleaching (Szubert *et al.,* 2006; Lizama *et al.*, 2003; Safari *et al.*, 2009 and Ndukwe and Uchendu, 2012). For a spherical particle involving a quasi-steady state diffusion of the reactant through the previously reacted portion of the particle, followed by chemical reaction at the surface of the unreacted core, equations (1), (2) and (3) are the integrated equations of the shrinking core model (Feng *et al*., 2015).

$$K_f t = X \qquad (1)$$

$$K_r t = 1 - (1 - X)^{1/3} \qquad (2)$$

$$K_d t = 1 - \frac{2}{3}X - (1 - X)^{2/3} \qquad (3)$$

The equations (1), (2) and (3) are for the film diffusion control mechanism, surface chemical reaction control mechanism and ash layer diffusion control mechanism respectively, where X is the conversion fraction of iron. K_f, K_r and K_d are the apparent rate constants for film diffusion, surface chemical reaction and diffusion through ash layer respectively and t is the contact time. In theory, any of these steps could be rate limiting.

Ndukwe and Uchendu (2012), used the shrinking core model to investigate the kinetics of bioleaching of iron from silica sand with *Aspergillus niger* and a contact time of 30 days. The study revealed that from day 15 to day 30, ash layer diffusion seemed to be in control, but it failed at the earlier stage of the bioleaching process.

Equation (4) is a mixed kinetic model which is a combination of the conversion terms of the chemical reaction model and ash layer diffusion model (Sultana *et al*., 2014)

$$K_m t = 1 - \frac{2}{3}X - (1 - X)^{2/3} + b\left(1 - (1 - X)^{1/3}\right) \qquad (4)$$

Where K_m = apparent rate constant

X = fraction of reacted particle

t = time of reaction

b = multiplying factor for chemical reaction

The change in proportion of the dominating reaction mechanism is established by setting the value of ‘b’ in the equation from between 0 and 1. By substituting each of the values of “b” into the equation and subsequently fitting to the linear model, the value of ‘b’ that produces the best fit is then used to determine the rate constant and the corresponding coefficient of determinations. The multiplying factor, b, is a direct function of chemical reaction control model. Hence, small value of b means that ash layer diffusion is the more dominant process while high value of b indicates that chemical reaction dominates.

Sultana *et al* (2014) have applied the mixed model (eqn 2.4) in a study aimed at establishing the kinetics of leaching of iron oxide clay in oxalic acid and Hydrochloric acid solutions. It was observed that neither ash layer diffusion control model nor the chemical reaction control model could describe satisfactorily the entire process. The experimental data however gave a satisfactory result when correlated with the mixed kinetic model. Two key observations were made: first was that the reaction followed mixed kinetic model and secondly, the ash layer diffusion was the most dominant reaction.

This work seeks to study the effect of particle size on the bioleaching of iron from silica sand using *Aspergillus niger* and an effort is made to correlate the data with mixed kinetic model in addition to the shrinking core models (SCM) which have earlier been studied by Ndukwe and Uchendu (2012).

2. MATERIALS AND METHODS

2.1 Sample Preparation and Identification of Iron in Silica Sand:

5kg of naturally occurring silica sand was obtained from Otammiri River in Owerri West L. G. A, Imo state, Nigeria. The sample was washed with deionized water to remove clay particles and other unwanted materials on the surface of the sand, after which it was dried for 3-days and separated into different particle size fractions with the aid of manual sieves. Five different particle size ranges which include +120 - 212µm, +212µm - 300µm, +300 - 425µm, +425 - 650µm and +650 - 1000µm were selected for the experiments. 0.5g of the dried silica sand was digested in concentrated Hydrochloric acid solution and evaporated nearly to dryness to remove excess acids. 5ml of 0.1M potassium permanganate solution were added to oxidize the iron to iron III state after which distilled water was added to make it up to 100cm^3. 40cm^3 of the solution was taken and put into a graduated flask. 5cm^3 of the thiocyanide solution and 3cm^3 of 4M Nitric acid were added and distilled water was used to make up the mark to 100cm^3. The colour of the solution changed to ox-blood, indicating the presence of iron in the sand.

2.2 Determination of Initial Concentration of Iron in Silica Sand:

Standard solutions containing 0.5 to 2.5mg/ml of Iron (III) were prepared and the absorbance of the solutions were determined with the aid of a UV/Visible spectrophotometer (Searchtech, 755S(UK)). These formed the standard solution data of fig. 1 and table 1. 2g of silica sand from the first particle size range (+120 -212µm) was weighed and transferred into a 250ml conical flask containing 25ml of 8M HNO_3 and made up to 100ml with distilled water. The mixture was agitated manually for about 5minutes and then subjected to digestion for about 60 minutes. The solution was cooled and then filtered into 100ml standard flask after which 10ml of it was pipetted and its absorbance was determined using uv/visible spectrophotometer (Searchtech, 755S(UK)) at a wavelength of 510nm. This experiment was repeated for the particle size range +212µm - 300µm, +300 - 425µm, +425 - 650µm and +650 - 1000µm. The results are given in table 2.

2.3 Fungi Isolation, cultivation and Identification:

The fungus was isolated from soil at a refuse dump in Owerii Municipal, Imo State. The culture Sabouraud Dextrose Agar (SDA) medium was prepared according to the manufacturer’s instruction. 62g of the SDA (TM MEDIA, India) was dissolved in 1000ml of distilled water and stirred thoroughly to ensure proper homogenization. It was allowed to soak for 10 minutes, mixed and sterilized by autoclaving at 121^{o}C for 15minutes and was cooled to 45^{0}C before pouring into sterile petri-dishes. 1g of the soil sample was weighed and dissolved in 9ml of sterilized formal saline. 0.1ml was pipetted out and spread evenly on solidified SDA, and incubated at 30^{0}C for about 7 days when adequate number of spores must have formed. The fungal isolate was identified based on its morphology and colour of the surface of the colony using fungal identification guidelines described by Samson *et al*, (2001). For microscopic identification, wet mounts of the isolate were prepared using lacto phenol cotton blue. A drop of the lacto phenol cotton blue was placed on a sterile grease-free slide with a sterile dissecting needle. A small portion of the inoculum was collected and tested on the slide. The sample was covered with a cover slip and examined under microscope to observe hypha cells and spores. The spore suspension was diluted with deionized water and standardized to 2 x 10^8 spores/ml of suspension.

2.4 Bioleaching Experiment:

2.0g of silica sand from the least particle size range, +120 - 212µm was weighed into 250ml conical flask containing 150ml of prepared medium which contains Sucrose, 100g/L; NH_4NO_3, 450mg/L; KH_2PO_4, 100mg/L; $MgSO_4.7H_2O$, 300mg/L; $FeSO_4.7H_2O$, 0.1mg/L; $ZnSO_4$, 0.25mg/L as culture medium (Cameselle *et al*, 2003). The medium and the silica sand sample were sterilized by autoclaving for 20minutes at a temperature of 121^{0}C after which 2ml of spore suspension (2 x 10^8 spores/ml) was introduced into the flask. The flask was plugged with non-absorbent cotton before sterilization in order to maintain aerobic condition (Basset *et al*, 1986). The flask was agitated initially for 30 minutes in an electric shaker at 150rpm in order to achieve a good degree of homogeneity. The pH of the medium was kept at 5.5 while temperature was maintained at 30±2^{0}C throughout the experiment. Subsequently, the mixture was shaken for 2 hours daily. The sample was monitored every day for 30 days. Every 3 days, 10ml of the leachate from the mixture was pipetted, filtered and digested to stop further microbial action. The concentration of iron leached out was determined with the aid of a uv/visible spectrophotometer (Searchtech, 755S (UK)) after which the fractional conversion of iron was calculated. This procedure was repeated for the particle size ranges +212µm - 300µm, +300 - 425µm, +425 - 650µm and +650 - 1000µm. The results are given in table 3. The fractional conversions have been plotted against time for each of the particle size ranges as shown in fig. 2.

2.5 Identification of Reaction Kinetics:

Since previous experiment showed that the particle size fraction +120-212µm were most suited for bioleaching, the data obtained with it were fitted to the shrinking core model, (Chemical reaction control equation and ash layer diffusion control equation) and mixed kinetic model. The rate constants K_r (chemical reaction control), K_d (ash layer diffusion control) and K_m (mixed kinetic model) obtained from the fit were used to predict the conversion fraction of iron based on the appropriate models. MATLAB Program was written to solve for fractional conversion, X, in each of the equations, 2 (chemical reaction), 3 (ash layer diffusion) and 4 (mixed model) with the right hand and left hand sides of each of the equations matched to a reasonable error margin. The best multiplying factor “b” in the mixed kinetic model for the +120-212µm particle size was 0.2 based on the highest coefficient of determination R^2. The results are given in table 5 and fig. 5.

3. RESULTS AND DISCUSSIONS

3.1 Particle Size:

Table 3 and fig. 2 show the variation of the fraction of iron leached out with time for each of the particle size ranges after a contact time of 30days. From fig. 2, it is seen that for each of the particle size ranges, the fraction of iron removed increased significantly with the contact time. However, on the average, the rate of bioleaching of iron with time increased steadily up to the 24th day. The curves became almost flat after the 27th day, showing that the bioleaching of iron was approaching equilibrium.

Also, the fraction of iron removed increased with decreased particle size all through the period of bioleaching. This may be attributed to the increase in surface area of the particles with decreased particle size. From table 4, the smallest particle size range (+120 - 212µm) recorded the highest fraction of iron removed (0.9750) which is an improvement of the earlier result obtained by Ndukwe and Uchendu (2012) who recovered 0.9678 fraction of iron from silica sand using the same microorganism, *Aspergellus niger*. It was only in the case of the smallest particle size (+120 –212 µm) that the process was able to reduce the concentration of iron in the silica sand to the permissible limit for production of some glass products (BSM, 1988). The overall percentage of iron removed with the size fraction was equivalent to a reduction of iron in the sand from 4.5% to 0.11%, which satisfies the British Standard Specifications for production of Grades F and G glass products. For the other particle sizes, the final % composition of iron in the silica sand still exceeded the permissible limits for all the seven grades of glass products according to the British Standard. Considering that the rate of bioleaching was near equilibrium after 27 days, the fungi used might not reduce the iron concentration of sand particles larger than +120-212µm to acceptable values even if exposed for a longer time. The implication is that larger size fractions will require coupling bioleaching to another process, e.g electromagnetic process, to reduce their iron contents to meet industrial specification for glass products. Our finding shows that size reduction circumvents this.

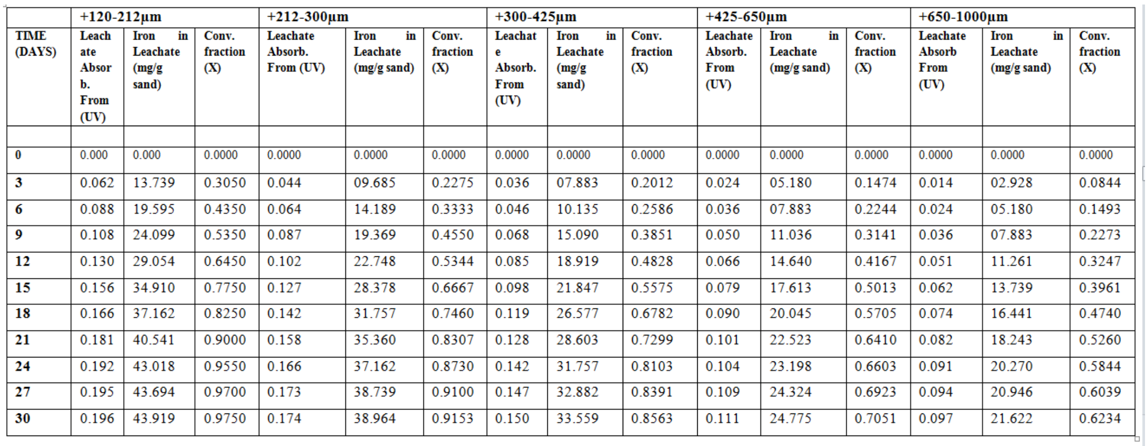
Table 1: Corresponding absorbance for the standard solution of Iron III

CONC. OF IRON III (mg/ml)	ABSORBANCE FROM UV SPEC
0.500	0.010
1.000	0.023
1.500	0.040
2.000	0.047
2.500	0.052

Table 2: Initial Concentrations of Iron in 2g Silica Sand of various Particle Sizes

PARTICLE SIZE (µm)	INITIAL CONC. OF IRON(mg/g sand)
+120-212µm	45.045
+212-300µm	42.568
+300-425µm	39.189
+425-650µm	35.135
+650-1000µm	34.685

Table 3: Variation of concentration of iron leached out from silica sand and fractional conversion with time for varying particle sizes at room temperature (≈ 30^{0}C)



	+120-212µm			+212-300µm			+300-425µm			+425-650µm			+650-1000µm		
TIME (DAYS)	Leachate Absorb. From (UV)	Iron in Leachate (mg/g sand)	Conv. fraction (X)	Leachate Absorb. From (UV)	Iron in Leachate (mg/g sand)	Conv. fraction (X)	Leachate Absorb. From (UV)	Iron in Leachate (mg/g sand)	Conv. fraction (X)	Leachate Absorb. From (UV)	Iron in Leachate (mg/g sand)	Conv. fraction (X)	Leachate Absorb From (UV)	Iron in Leachate (mg/g sand)	Conv. fraction (X)
0	0.000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
3	0.062	13.739	0.3050	0.044	09.685	0.2275	0.036	07.883	0.2012	0.024	05.180	0.1474	0.014	02.928	0.0844
6	0.088	19.595	0.4350	0.064	14.189	0.3333	0.046	10.135	0.2586	0.036	07.883	0.2244	0.024	05.180	0.1493
9	0.108	24.099	0.5350	0.087	19.369	0.4550	0.068	15.090	0.3851	0.050	11.036	0.3141	0.036	07.883	0.2273
12	0.130	29.054	0.6450	0.102	22.748	0.5344	0.085	18.919	0.4828	0.066	14.640	0.4167	0.051	11.261	0.3247
15	0.156	34.910	0.7750	0.127	28.378	0.6667	0.098	21.847	0.5575	0.079	17.613	0.5013	0.062	13.739	0.3961
18	0.166	37.162	0.8250	0.142	31.757	0.7460	0.119	26.577	0.6782	0.090	20.045	0.5705	0.074	16.441	0.4740
21	0.181	40.541	0.9000	0.158	35.360	0.8307	0.128	28.603	0.7299	0.101	22.523	0.6410	0.082	18.243	0.5260
24	0.192	43.018	0.9550	0.166	37.162	0.8730	0.142	31.757	0.8103	0.104	23.198	0.6603	0.091	20.270	0.5844
27	0.195	43.694	0.9700	0.173	38.739	0.9100	0.147	32.882	0.8391	0.109	24.324	0.6923	0.094	20.946	0.6039
30	0.196	43.919	0.9750	0.174	38.964	0.9153	0.150	33.559	0.8563	0.111	24.775	0.7051	0.097	21.622	0.6234

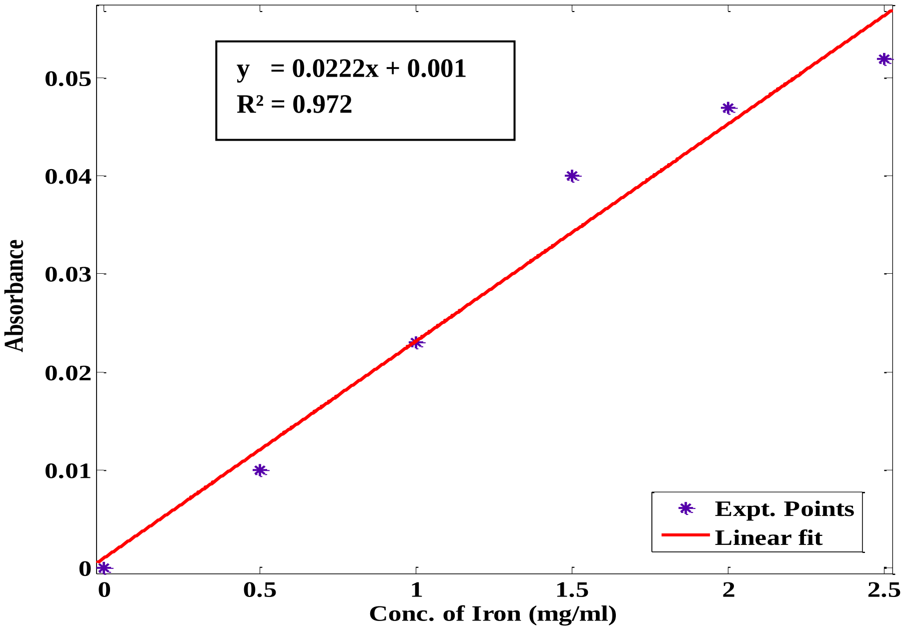


Fig. 1: Variation of Absorbance with Concentration of Iron in the Standard Solutions of Iron III

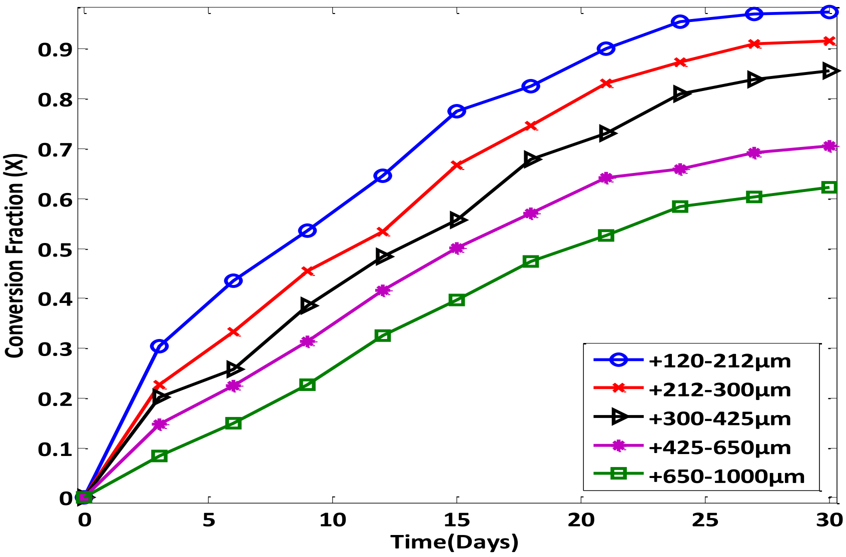


Fig. 2: Fraction of Iron leached versus Time for varying Particle Sizes

Table 4: Initial and Final Concentrations of Iron in the Silica Sand after 30 days

Particle Size (μm)	Initial Conc. Of Iron in Silica Sand (mg/g)	Overall Conc. Of Iron in leachate (mg/g)	Final Conc. Of Iron In Silica Sand (mg/g)	Overall Fraction Of Iron leached out	Initial % Composition of Iron In Silica Sand (%)	Final % Composition of Iron In Silica Sand (%)
+120 –212	45.045	43.919	1.126	0.9750	4.50	0.110
+212 –300	42.568	38.964	3.604	0.9153	4.26	0.360
+300 –425	39.189	33.559	5.630	0.8563	3.92	0.560
+425 –650	35.135	24.775	10.360	0.7051	3.51	1.040
+650 –1000	34.685	21.622	13.063	0.6234	3.47	1.310

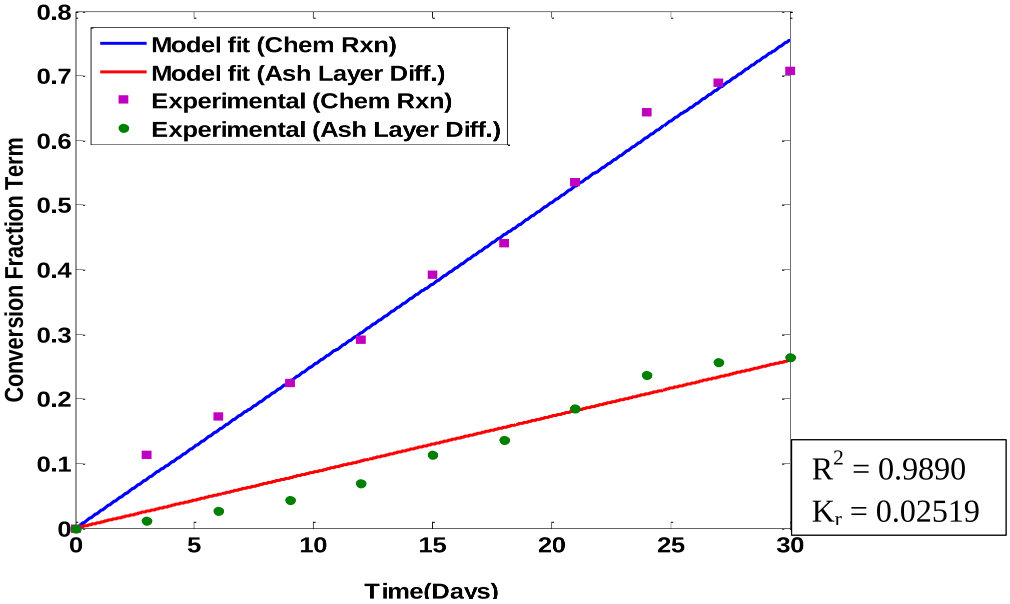


Fig. 3: Fractional Conversion Term versus Time for the Particle Size +120-212µm at Room Temperature (30^{0}C) (Chemical Reaction and Ash Layer Diffusion Model)

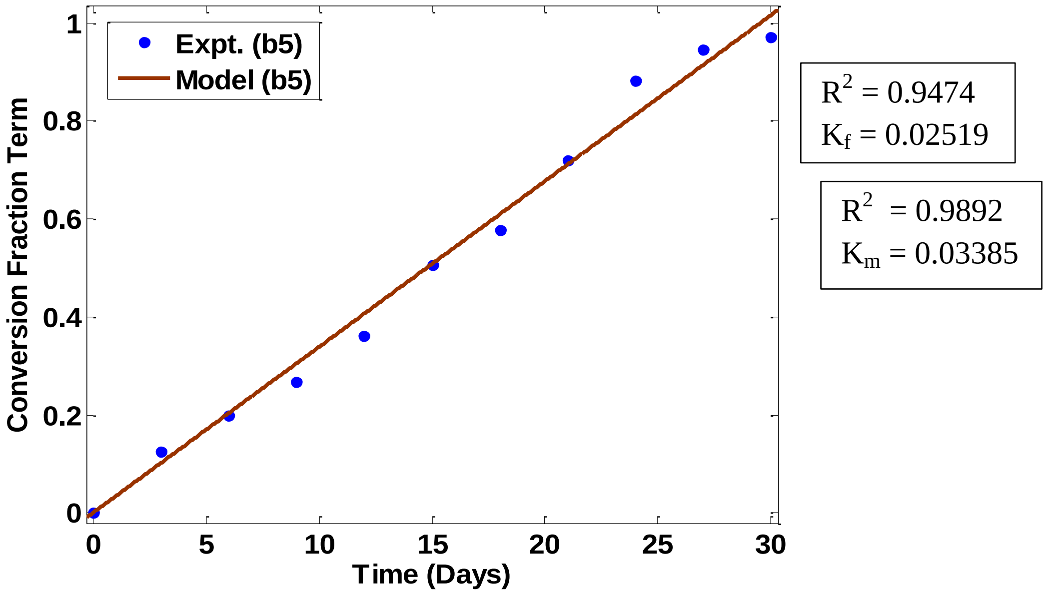


Fig. 4: Conversion Fraction Term versus Time for Particle Size +120 - 212µm at Room Temperature (Mixed Kinetic Model)

Table 5: Fractional Conversion predicted by the Ash Layer Diffusion Model, Chemical Reaction Model and the Mixed Model with the Experimental Fractional Conversion for the particle size range of +120-212µm at room temperature (30^{0}C)

Time (Days)	**Conv. fract. ($X_{expt.}$)**	**Conv. fract. ($X_{pred.}$) Ash Layer**	**Conv. fract ($X_{pred.}$) Chem. Rxn**	**Conv. fract. ($X_{pred.}$)Mixed Model**
0	**0.0000**	0.0000	0.0000	0.0000
3	**0.3050**	0.4308	0.2100	0.2575
6	**0.4350**	0.5775	0.3883	0.4442
9	**0.5813**	0.6771	0.5376	0.5860
12	**0.6910**	0.7519	0.6603	0.6959

15	**0.7750**	0.8108	0.7592	0.7817
18	**0.8440**	0.8581	0.8367	0.8485
21	**0.9000**	0.8964	0.8955	0.8998
24	**0.9275**	0.9275	0.9382	0.9382
27	**0.9700**	0.9525	0.9673	0.9657
30	**0.9750**	0.9720	0.9854	0.9840

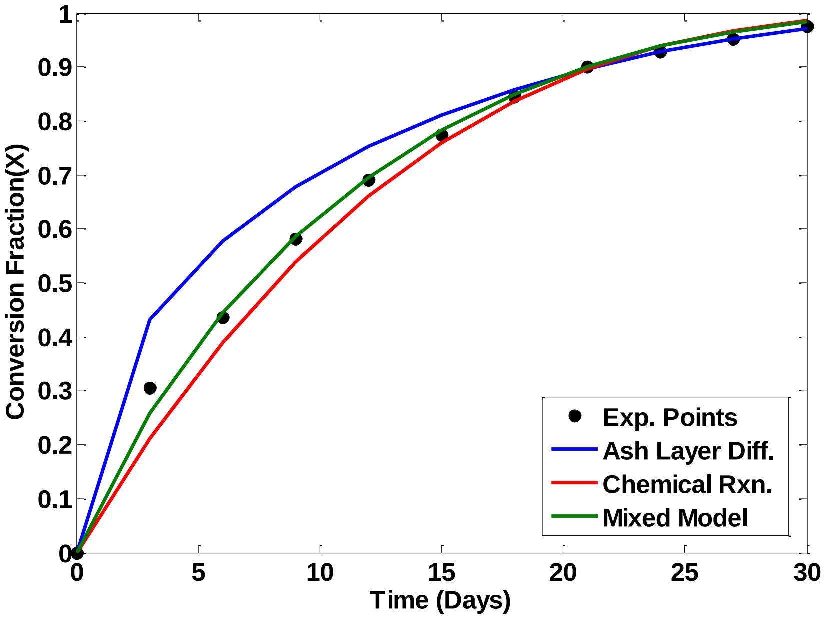


Fig. 5: Comparison of the Experimental Conversion Fraction (X_{exp}) versus Time t, with the predicted Conversion Fraction ($X_{pred.}$) for Particle Size

3.2 Reaction Kinetics:

From fig. 5, the predictions of the chemical reaction controlled shrinking core equation did not match the experimental data. Hence, chemical reaction is not rate limiting. Ash layer diffusion seems to be in control from day 21 of the process to the 30th day. The agreement between the predicted data and the experimental data within this period (21st – 30th day) is very good. However, ash layer failed at the initial stage of bioleaching especially between day 1 and day 21.

The failure of the ash layer diffusion controlled shrinking core equation at the initial stages of bioleaching had been noticed by Lizama *et al* (2003) who ascribed it to bacterial cell colonization on the surface of the ore. Ndukwe and Uchendu (2012) in a separate work involving the use of *Aspergillus niger* for the bioleaching of iron from silica sand, made similar observation but stated that it was not certain if the reason given by Lizama *et al* (2003) applies to fungi.

The figure further reveals that for the mixed kinetic model, the agreement between the predicted data and the experimental is quite good as from the 6th day of bioleaching to the 21st day. However, the model slightly deviated from the experimental data after the 21st day of bioleaching. It can be said therefore that the process followed mixed kinetic model from 6th to 21st day of bioleaching while ash layer diffusion controlled the process from 21st day to the 30th day of the bioleaching. It follows that none of the models described perfectly, the process from the first to the last day of bioleaching. The mixed model is much better than the chemical reaction or the ash layer diffusion model.

4. CONCLUSION

Particle size has been found to exert significant effects on the bioleaching. At room temperature (30^{0}C), leaching increased with decreased particle size and the least particle size (+120-212μm) met the requirement for production of grades F and G glass products. This corresponds to a reduction in the %composition of iron in the silica sand from 4.5% to 0.11%. There may be some sense in implementing size reduction of silica sand by mechanical means prior to heap leaching in the industry with fungi.

The mixed model fitted the experimental data very well from day 6 to day 21; the chemical reaction and ash layer diffusion models failed within this range. The fit to the bioleaching data between day 21 and day 30 by the mixed model was fair, but the ash layer diffusion model was very good in this range. The mixed kinetic model and the ash layer diffusion model may be integrated in the design of the bioreactor for the bioleaching of iron from silica sand with *Aspergeillus niger.*

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