Physical Sciences

HYDROCHLORIC ACID LEACHING OF MINERALS FROM NIGERIAN SOIL

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Effects of particle size on the leaching of some metals (Mn, Cu, Fe and Zn) from soil was studied at room temperature and different hydrochloric acid concentrations. It was found that the metal concentration in the leachate decreases steadily with increasing leaching time up to a limit with exception of iron. However, the metal concentration observed at 75μm and 288μm did not differ largely after a long time of leaching. The highest metal concentration was obtained using a particle size of 75μm. A linear relationship was established between the plots of inverse of concentration in the leachate and inverse of leaching time. This observation confirms the validity of the proposed equation for the correlation of the concentration in the leachate with leaching time. The correlation of the predicted leaching concentrations with the experimentally determined ones showed only 11.0% deviation.

Key words: Leachate, Soil, Minerals.

Introduction

Many cations are found in soils. These cations play a major role in the retention of organic matter in fixation processes in many soils and in supplying adequate minerals for the plant. The importance of minerals as nutrients for both plants and animals cannot be over emphasized. Elements are essential to produce enough enzymes to catalyze essential plant processes. For example, copper serves as co-enzyme in oxidation - reduction processes of plant metabolism. Deficiencies of some of the minerals can lead to abnormal plant development and poor yield. A knowledge of minerals in soil can help in determining the type of inorganic fertilizer to be applied to plants grown on such soils. It also provides the extent to which the soil is polluted with heavy metal.

The leaching of minerals from laterite and ilmenite by the use of acid solutions has been widely reported (Oderinde and Olanipekun, 1992a; Olanipekun et al 1993). Hydrochloric and sulphuric acid extraction of ions (Na, K, Ca, P, and N) from fresh and dried soils have also been reported. (Gilliam and Richler 1988). Also reported is the single extraction of iron from soil samples and clays (Coffin 1963). There is no reported work on the leaching of heavy metals from Nigerian local soils. The removal of heavy metals from the soil is important to the mineralogical examination of soil particles. The present study was therefore undertaken to investigate factors (like concentration; particle size and time) that can affect the leaching process.

Experimental

The representative soil sample was obtained from an arable farm land from Oba-Ile, Akure, Ondo State, Nigeria. The soil
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sample was milled and sieved into the desired particle sizes. The samples with the desired particle size (75, 288 and 675μm) were packed in polythene bags and kept for analyses and leaching experiments.

Two grams of the soil with the desired particle size was leached with hydrochloric acid. The detailed experimental technique has been fully described by Oderinde and Olanipekun (1992b). The mixture was continuously stirred with a magnetic stirrer to minimise or eliminate the effect of external mass transfer. After the required time, the mixture was centrifuged and filtered and the filtrate stored for mineral analyses.

The desired minerals in filtrate were determined using the atomic absorption spectrophotometry. The values reported are average of two or more determinations.

Results and Discussion

The effect of particle size on the leaching of some metals (Mn, Cu, Fe, and Zn) from soils was studied at room temperature and different HCl concentrations.

Experiments were carried out with various particle sizes using large solution volumes with the result that the HCl concentration did not change significantly during any of the experiments. Typical curves obtained are shown in figures 1-4 for iron and copper leached in 0.1M HCl and Mn and Zn leached in 0.5M HCl. Similar curves have been obtained for the leaching of ilmenite using HCl solutions (Oderinde and Olanipekun 1992c).

The concentration of other metals leached (Cu and Zn) at both acid concentrations and different particle sizes followed the same pattern. From the curves, it was observed that the metal concentration in the leachate decreases steadily

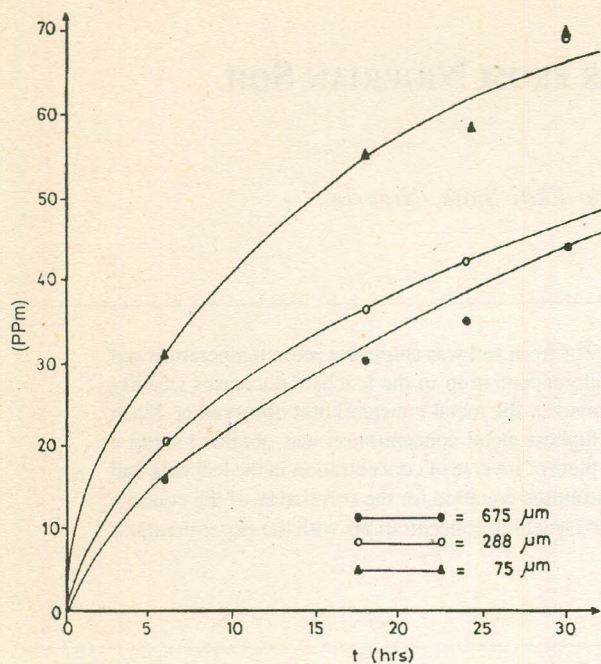O Olaofe, S S Asaolu, E O Olanipekun, J B Fatuase

Fig 1. Effect of leaching time and particle size on iron concentration in the leachate.
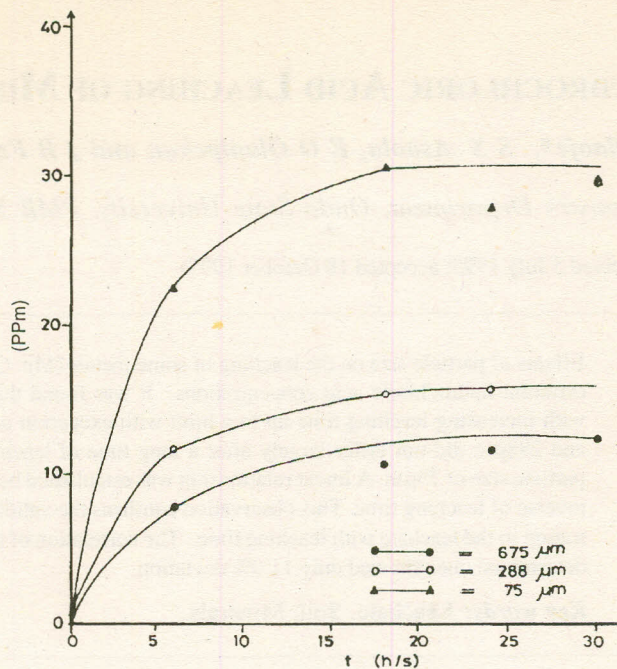

Fig 2. Effect of leaching time and particle size on manganese concentration in the leachate.
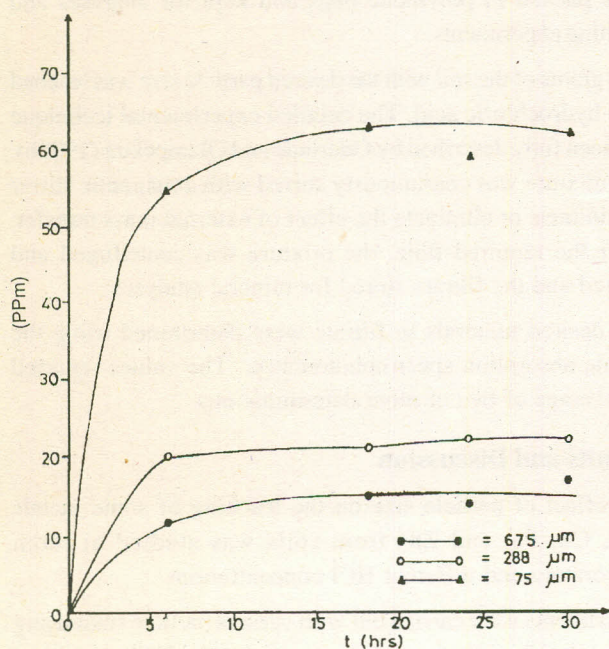

Fig 3. Effect of leaching time and particle size on copper concentration in the leachate.
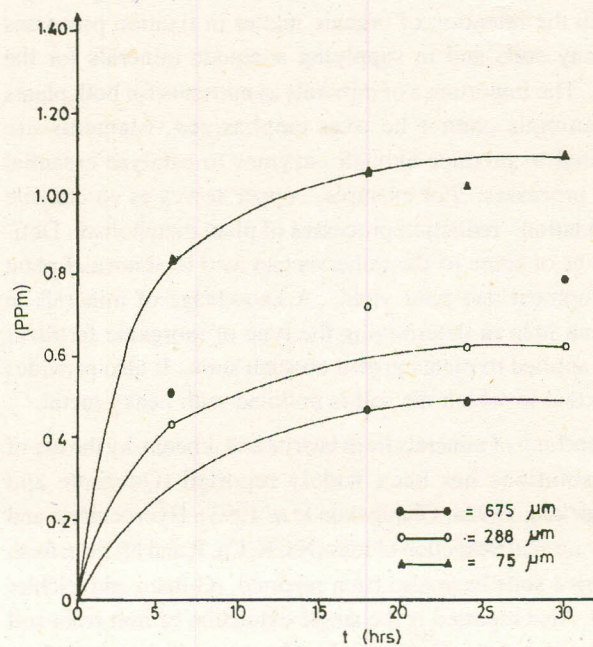

Fig 4. Effect of leaching time and particle size on zinc concentration in the leachate.

with increasing particle size, not differing largely at 75μm and 288μm but showing over 50% decrease when particle size was increased to 675μm. This is due to smaller surface area available for reaction to occur. Oderinde and Olanipe-kun (1992a,b) have also found that rate of extraction of metals from laterite and ilmenite in HCl with smaller particles is greater than using

bigger particle size. From this experiment, the highest metal concentration was obtained using a particle size of 75μm, and that was the optimum in this study. Similar results were obtained for other metals leached.

The effect of time on the leaching was also investigated and four of such results obtained are presented in figures1-4. Fig-

ures 1 and 3 show the variation of iron and copper concentration with time at room temperature and various particle sizes in 0.1M HCl; while figures 2 and 4 show the concentration of Mn and Zn with time at room temperature (20°C) at various particle sizes in 0.5M HCl. Generally, the metal concentration in the leachate increases with increasing time. The concentration steadily increases up to about 18 h after which the metal concentration apparently does not increase further with exception of iron in figure 1 implying that no significant leaching of either of the four metals occurs again after 18 h optimum time. The present observation shows that an equilibrium has been established between the concentration in the solution and soil (Draper and Smith 1966).

The equation below is being proposed to predict the concentration of metal leached at a particular time t. Similar equation has been used to predict the absorption of molecules in solution (Walter and Webber 1955).

$$C = \frac{K_1 t}{1 + K_2 t} \qquad \text{............................. (1)}$$

Where C = concentration of metal
   t = leaching time
   K_1 and K_2 are constants.

Linearizing equation (1) above gives equation (2) below:

$$\frac{1}{C} = \frac{1}{K_1 t} + \frac{K_2}{K_1} \qquad \text{............................. (2)}$$

A plot of 1/C against 1/t is expected to give a straight line graph with slope of $1/K_1$ and intercept K_2/K_1, from where K_1 and K_2 can be calculated.

In order to test the validity of the proposed equations, the reciprocal of the concentration of the various metals leached was plotted against the reciprocal of the reaction time and typical results are shown in figure 5. The plots showed linear relationship between 1/C and 1/t. This confirms the validity of our proposed equation. It therefore follows that using the equation, the concentration of metals leached from soil at time t can be predicted.

Table 1 shows a summary of the values of K_1 and K_2. The concentrations predicted were then plotted against the experimentally determined concentrations and the result is shown in figure 6. The percentage deviation of the C_{obs} from the C_{pred} was calculated using the expression (Draper and Smith 1966).

$$\% \text{ Deviation} = \Sigma \; \frac{(/C_{pred'} i - C_{obs'} i /)}{C_{obs'} i} \; X \frac{100}{n}$$

Where C_{pred} = predicted concentration
   C_{obs} = observed concentration.
   n = number of experiments

Table 1
Summary of the parameters K_1 and K_2 in the proposed equation 1

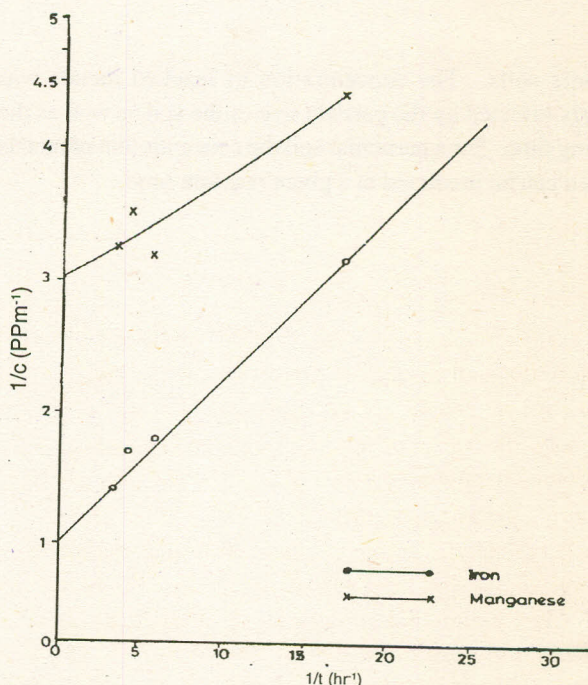| Acid concentration | | HCl concentration | | | |
| Particle size(μm) | Minerals | 0.1M | | 0.5M | |
		K_1	K_2	K_1	K_2
75	Mn	18	0.75	12	0.38
	Fe	1.3	0.60	7.9	0.08
	.Cu	0.22	0.30	0.43	0.34
	Zn	5.1	2.1	0.55	0.89
288	Mn	9.5	0.52	3.1	0.11
	Fe	1.4	0.11	1.4	0.06
	Cu	24	130	0.33	0.15
	Zn	26	14	0.16	0.19
675	Mn	24	1.7	2.9	0.19
	Fe	1.5	0.12	3.9	0.07
	Cu	0.08	0.67	0.07	0.37
	Zn	1.50	0.77	0.36	0.54

Fig 5. The inverse of acid leached concentration against the inverse of leachin time.

In our case, n = 32, therefore % deviation is 11.0%. This value shows that there was a satisfactory agreement between the predicted and the observed concentration (Shczynski *et al* 1991). This suggests that the proposed equation can be used for design purposes.

In conclusion, this study has shown that leaching of iron, copper, manganese and zinc would occur significantly mostly
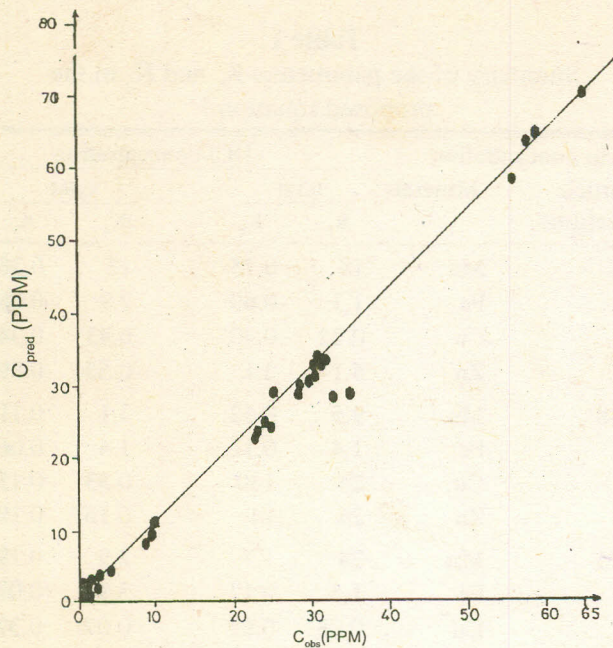
Fig 6. The experimentally determined leached mineral concentrations against theoretically predicted leached mineral concentrations.

in acidic soils. The concentration of leached metals was strongly affected by the particle size of the soil as well as the leaching time. For a particular soil the concentration of metals leached can be predicted at a given reaction time.

References

Coffin D E 1963 A method for the determination of free iron in soils and clays. *Can J Soil Sci* **43** 7-17.

Draper N R, Smith H 1966 *Applied Regression Analysis,* John Wiley and Sons.

Gilliam F S, Richler D D 1988 Correlations between extractable Na, K, Mg, Ca, P and N from fresh and dried samples of two Aguuits. *J Soil Sci* **39** 209-214.

Oderinde R A, Olanipekun E O 1992a Kinetics of hydrochloric acid leaching of laterite. *Pak J Sci Ind Res* **35** (3) 77-80.

Oderinde R A, Olanipekun E O 1992b Effect of sulphate on the kinetics of leaching of laterite by hydrochloric acid. *Ghana J Chem* **116,** 277-283.

Oderinde R A, Olanipekun E O 1992c Chemical beneficiation of Nigerian ilmenite ore. Part I. Hydrochloric acid. *Pak J Sci Ind Res* **35** (7&8) 313-316.

Olanipekun E O, Oderinde R A, Okurumeh O K 1993 Leaching of ilmenite in phosphoric acid. *Trans Indian Inst Met* **46**(1) 45-47.

Shczynski J, Grabowski R, Janes J 1991 Adsorption model of methanol on CuO-ZnO Al_2O_3 Catalysts-II. Adsorption of the individual components on the catalyst. *Chem Engg Sci* **46**(10) 2611.

Walter J, Webber H 1955 *Adsorption Theory, Concept and Models. Adsorption Technology*, ed Slejko FL, Marcel Debber & Son, Chapter 1, pp 1-35.