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ANALYSIS OF SLUDGE USING PROTON INDUCED X-RAY EMISSION

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ABSTRACT

Regulations to control the huge amounts of sludge produced by wastewater are needed. Sludge generated in conventional sedimentators or anaerobic digestors were characterized by Proton Induced X-ray Emission (PIXE). It was possible to determine the presence of macronutrient elements, such as P and K, and secondary nutrients like Ca, S, and Mg. Moreover, heavy elements like Cu, Zn, and Pb were also found. The sludge treatment in anaerobic digestors increased the amount of certain elements Al, Si, S, Cl, and K; decrease in Ca, Ti, and Cu, and no change in V, Cr, and Zn. Possible uses of this sludge are also suggested.

RESUMEN

El trabajo está orientado a la búsqueda de estrategias para la adecuada disposición de los lodos provenientes del tratamiento de aguas residuales de origen doméstico. Después de ser manejado el lodo en un digestor anaeróbico durante diferentes períodos, se caracterizó mediante análisis elemental empleando la técnica de emisión de rayos X inducidos por protones (PIXE). Con relación a la posibilidad de utilizar los lodos para cultivo de plantas, en los estudios realizados, se estableció la presencia de macronutrientes como P y K, además de nutrientes secundarios como Ca, S y Mg. Se encontraron también metales pesados como Cu, Zn y Pb. Se analizó estadísticamente el efecto que sobre la concentración tiene el tiempo de tratamiento de los lodos en el digestor, obteniéndose el enriquecimiento en Al, Si, S, Cl y K, el empobrecimiento en Ca, Ti y Cu, mientras que para V, Cr y Zn no se observaron cambios significativos.

INTRODUCTION

Wastewater, either from industrial origin or from domestic use, is an important polluting agent, as it carriers toxic elements that may cause ecological disorders if it is not conveniently handled. The heavy metals content, even at low concentrations, may represent a health risk. The Mexico City Metropolitan Zone (MCMZ) is one of the most rapidly growing areas in the world, with a population approaching 20 million inhabitants. According to data published by the National Hydraulic Plan (1990) the MCMZ produced 3.60×10^9 m^3 a year of wastewater, which in turn generated 8.85×10^5 ton of dry sludge containing pathogenic organisms, high content of organic matter and several toxic compounds. In some cases, wastewater produced in urban zones is used to irrigate agricultural areas (Flores-Delgadillo *et al.* 1992). Searching for ways to ameliorate the damage of the wastewater use, different procedures for decontamination and control have been implemented. The reuse of these wastewaters in industrial areas is also being studied. In this context, the Environmental Engineering Section, of the Engineering Faculty at the Universidad Nacional Autónoma de México, designed and constructed conventional anaerobic "digestors," (Möeller and Soler 1993) for the treatment of "primary" sludge produced by the primary sedimentator of the wastewater treatment plant in Chapultepec, within the limits of the MCMZ, which is intended for domestic reuse of water. With these digestors, a possible sludge stabilization is explored while reducing the retention time in the digestors under the restriction that contamination levels are always kept below those imposed by the regulations. Following this method, the sludge may be reused for agricultural purposes and not simply eliminated through the pipelines or dumped elsewhere as it is usually done nowadays thus causing contamination of the receptor system.

On the other hand, reliable determination of the pollutants in sludge is necessary in order to develop appropriate methods for the handling and use of the sludge. If possible, fast and sensitive procedures for the analysis should be followed. This is the case of Proton Induced X-ray Emission (PIXE) (Johansson and Campbell 1988), which is an analytical technique that gives simultaneous information on most elements having atomic number higher than 12 and with sensitivities as low as one part in 10^9, depending on the element, sample type, and preparation. PIXE spectrometry is based on the X-rays produced after ionization of the inner shells of the target atoms under irradiation by protons. The resulting X-ray spectrum is used to carry out quantitative analysis of all the elements heavier than Mg that are present in the sample. In this work, PIXE analysis results of sludge from the digestors mentioned above are presented. The result is discussed to compare the performance of two digestors and to evaluate uses of the sludge based on this characterization.

MATERIALS AND METHODS

Wastewater is initially treated in a primary sedimentator. Forty samples of the resulting sedimented sludge (influent) were taken randomly during a period of one year. For the studies, we never considered more than one sample a day. Part of each one of those samples was directly processed during 7 days in an anaerobic digestor (Soler *et al.* 1992). 20 of the 40 sedimented sludge samples, were processed in the same digestor for 14 days. That way it was possible to fabricate 40 targets for influent (without processing), 40 targets for reactor 1 (7 days) and 20 targets for reactor 2 (14 days). We considered two different periods to try to determine the minimum time required to reach a stabilization, which means, the disappearance of odors, partial destruction of solid matter, reduction of pathogenic microorganisms and the avoidance of spontaneous biological degradation once the treatment has been finished.

The operation of an anaerobic reactor is based on the process of methanogenesis, which is a biological anaerobic method consisting of the progressive degradation of organic matter by means of microorganisms presenting as an important consequence from an energetic viewpoint the production of methane (Malina and Pohland 1992).

The resulting stabilized sludge was dried, ground and homogenized until a representative residual sample was obtained. The samples to be irradiated with protons were made by finely grinding the sludge in an agate mortar and depositing them on 3.5 μm thick Mylar films previously impregnated with a solution of toluene and Apiezon vacuum grease (Gill 1989). The mass deposited on these films was determined by weighing the film before and after the material deposition. An average sample thickness of 1 mg/cm^2 was obtained.

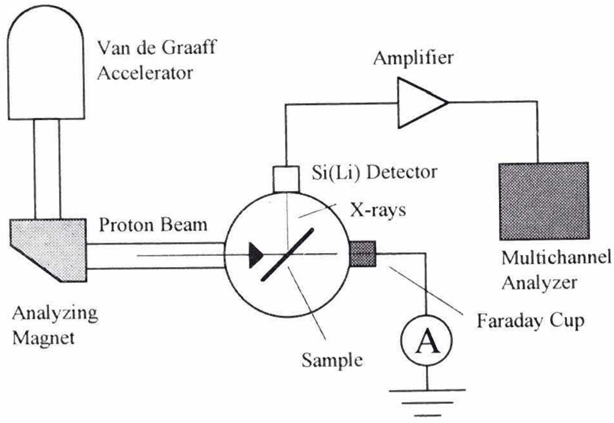

Figure 1. Diagram of the experimental setup for PIXE analysis

Figure 1 shows the experimental arrangement for the irradiation of the samples. A 1.8 MeV proton beam was produced by the 5.5 MV Van de Graaff accelerator at the Instituto de Física, UNAM. A 7.5 μm thick Kapton window was placed between the beam line and the scattering chamber and another between the chamber and the Si(Li) X-ray detector. The former to produce an homogeneous beam and the latter to reduce the number of X-ray photons reaching the detector. The detector had a resolution of 180 eV at 5.9

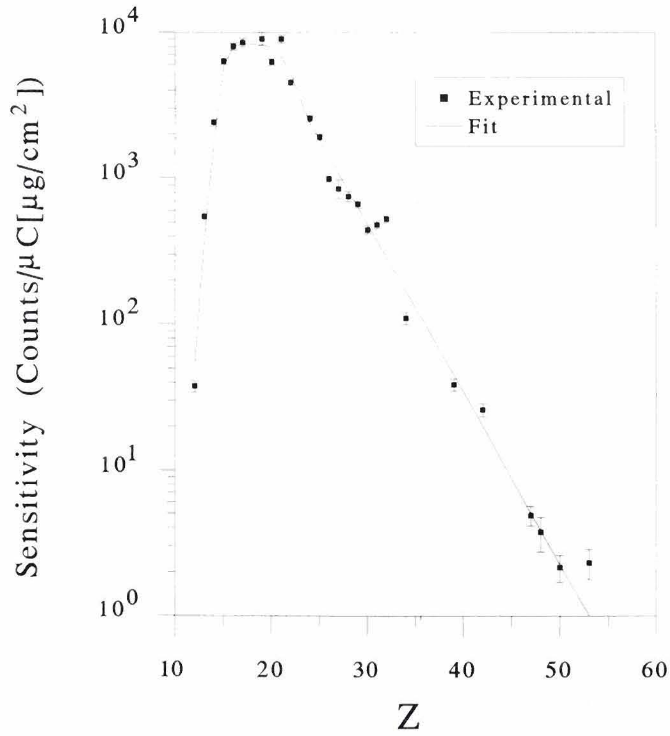

Figure 2. Sensitivity curve obtained for the detection system used in the PIXE analysis of sludge

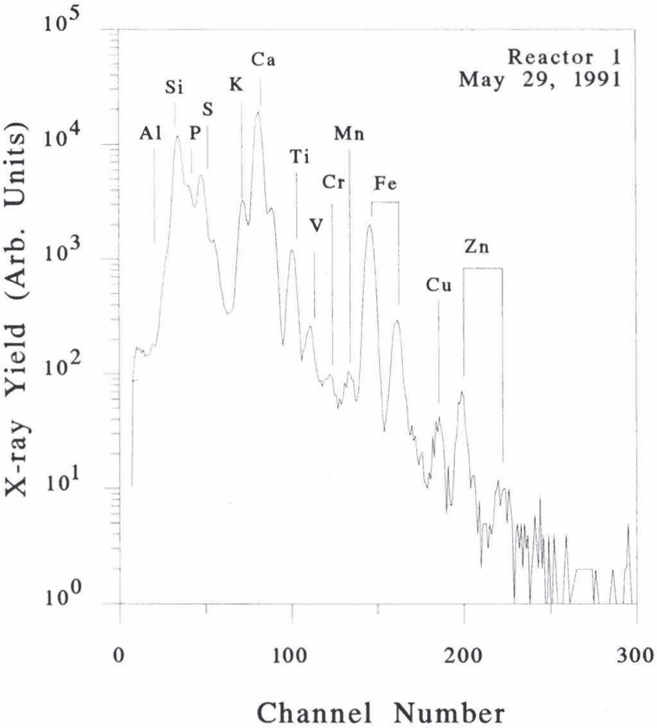

Figure 3. PIXE spectrum of one of the samples of sludge

keV. The angle between the surface of the sample and the incoming proton beam was 45°, while the detector was placed at 90° from the beam direction. During the irradiation, the X-ray photon count rate was always kept below 1500 counts per second to avoid pile-up effects and the total accumulated charge was normally 2.5 μC per sample. The sensitivity curve used for quantitative analysis (**Fig. 2**) was obtained by means of MicroMatter thin film standards.

ANALYSIS

Figure 3 shows a typical X-ray spectrum produced by the irradiation of the sludge. The computer code AXIL (Malina and Pohland 1992) was used to identify the X-ray lines and deconvolute the spectra.

The elemental concentration C was evaluated in a first approximation employing the equation:

$$c = \frac{Nx}{SQD} \tag{1}$$

where N_X (number of counts) is the peak area corresponding to a specific element, S (number of counts per μC per g/cm²) is the detection sensitivity for that particular element, Q (in μC) is the total accumulated proton charge, and D is the areal mass density of the sample (in μg/cm²).

As Eq. (1) is based on the assumption that the targets are negligibly thin it becomes necessary to calculate a correction factor f_M, due to stopping of the protons in the target and attenuation of the X-rays produced by the sample itself (Maenhaut *et al.* 1980). This matrix correction factor for a typical sample (Reactor 1, May 29, 1991), with a thickness t of 1.12 mg/cm² is shown in **figure 4**. It must be noted that there is a strong increase in f_M for P. The reason for this effect is that Si is the most important component of the sludge and the P X-rays lie just above the K absorption edge of Si. Moreover, when the X-ray energy increases the correction factor f_M decreases.

RESULTS

Table I shows the elemental concentrations found in the

TABLE I. AVERAGE CONCENTRATIONS (μg/g) AND PROBABILITY $(-\infty, t]$ FOR THE TEST $H_0: \mu_1=\mu_2$

	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Cu	Zn	Pb
Influent																
AVG*	34400	21900	60500	8600	6000	890	2020	14600	1460	61	73	310	8360	290	590	370
STD*	24300	11100	29700	4300	2990	550	990	6700	710	13	33	550	4240	130	260	170
N*	4	28	29	29	29	29	29	29	29	7	8	23	29	26	29	4
Reactor 1																
AVG		24500	67600	9900	7100	1500	2500	17200	1600	66	48	200	9000	290	660	360
STD		10600	29700	5300	3000	1500	1300	9100	690	32	28	96	4200	120	270	140
N		33	33	33	33	33	33	33	33	4	7	33	33	31	33	2
Reactor 2																
AVG	43600	25900	73600	9800	7300	1200	2300	14900	1600	45	55	220	9400	290	660	310
STD	4200	9700	28500	3200	2500	420	850	6400	650	20	46	58	3900	110	250	60
N	2	13	13	13	13	13	13	13	13	5	4	12	13	13	13	3
P(-,t)																
Inf-R1		0.18	0.18	0.14	0.09	0.02	0.04	0.11	0.21	0.37	0.92	0.85	0.27	0.63	0.17	0.53
Inf-R2	0.34	0.14	0.10	0.18	0.10	0.06	0.19	0.46	0.22	0.92	0.75	0.71	0.23	0.53	0.23	0.67
R1-R2		0.34	0.27	0.53	0.41	0.78	0.71	0.79	0.43	0.84	0.39	0.32	0.39	0.42	0.50	0.64

*AVG = Average, STD = Standard deviation, N = number of appearances samples. The provenance of the samples (Influent, Reactors 1 and 2), average values (AVG), percentile standard deviations (STD), and number of samples (N) in which the element was found, are also displayed. The reliability of sludge elemental concentrations obtained by PIXE analysis depends on a relatively large ratio between the range of protons and the particle size of the sample (SPEX, 1991). In order to test this requirement, if we consider a thick target constituted by the elements listed in **table I**, in proportions equal to the averages stated there and complemented with an oxygen matriz, by energy loss calculations we obtain 28 µm range for 1.8 MeV protons in this target. Due to their origin, wastewater pollutans are constituted by sulfates, silicates, aluminates, etc., which, taking the (approximate) atomic proportions given in **table I**, into account must probably contain such compounds as:

SiO_2, SO_3, $MgSO_36H_2O$, $MgSO_4$, $Al_2(SO_4)_3$ y $Ca_3Mg(SiO_4)_2$

Thus, a possibility to estimate the target density is to assume that the bulk is made from the individual (isolated) densities of these compounds taken in proportions in agreement to statistical weights determined by the molecular weights and concentrations of the major elements of the composite. In this way, we obtained 2.86 g/cm³ for the mean

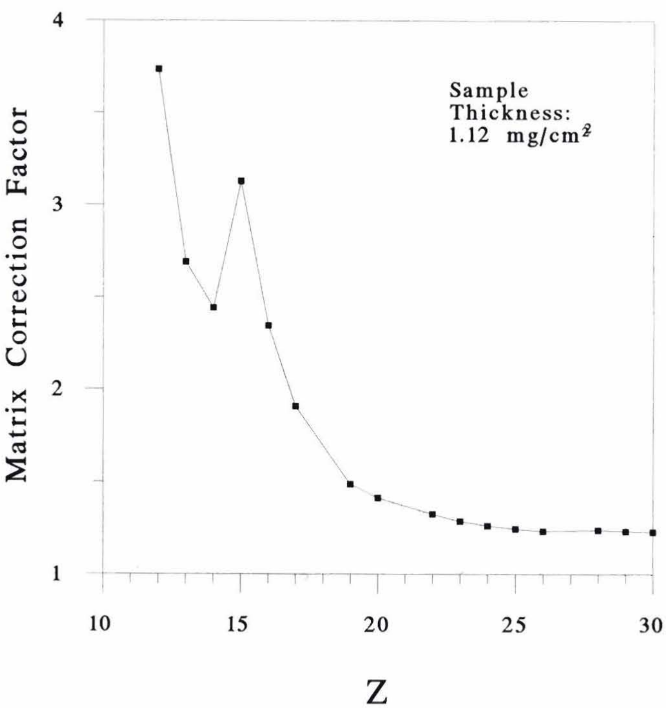

Figure 4. Matrix correction factor fM as a function of atomic number, for a sample of sludge with a typical mass thickness of 1.12 mg/cm²

$$t = \frac{\bar{X}_1 - \bar{X}_2}{\sqrt{\frac{1}{N_1} + \frac{1}{N_2}}} \quad \text{con} \quad \sigma = \sqrt{\frac{N_1 S_1^2 + N_2 S_2^2}{N_1 + N_2 - 2}} \tag{2}$$

where $\bar{X}$, S and N, are the mean, standard deviation and the size of the sample, respectively.

TABLE II. EFFECT OF RETENTION TIME IN A DIGESTOR RELATIVE TO INITIAL CONCENTRATION IN INFLUENT

Element	Change After 7 d	After 14 d	After 7-14 d
Si		22 (20%)*	
P		21 (20%)	0 (6%)
S	17 (4%)		
Cl	71 (4%)	31 (20%)	
K	26 (8%)		
Ca		0 (8%)	
V		-26 (16%)	
Cr	-34 (16%)		
Cu		0 (6%)	
Zn			0 (1%)
Pb	0 (6%)		

*Maximum error for statistical test in parenthesis

target density, which made it possible to estimate a target thickness of x = ~ 4 µm (where, $x\rho$ = 1.12 mg/cm²). Besides, through direct observation with an optical microscope, a 5 mm maximum grain size was measured for a sludge sample taken for this purpose. Using 4 mm as the maximum particle size for the sludge samples, we obtained a minimum ratio of 7:1 between the range of protons and the considered particle size. Maenhaut *et al.* (1980) obtained an accuracy and precision of 5% for PIXE in similar targets, without taking into account the particle size distribution (Maenhaut *et al.* 1987).

In **table I**, the calculated values of the probability $P(-\infty, t]$ for statistical testing of the equality of averages $H_0 : \mu_1 = \mu_2$. t is Gosset's variable; this value is determined by the mean values, deviations and number of data corresponding to two sets of values from Influent, Reactor 1 or Reactor 2 (ec. 2) for a given element. The effect of the retention times in the reactors on the elemental concentrations can be deduced from the values of t. This is summarized in **table II**, where the equality of averages is tested for an 80% significance and inequality for a 20% significance.

Two major aspects shown in **table II** must be pointed out. There is no significant effect on the elemental concentrations after a 14-days treatment for Influent in the digestor, except for Cr and V that showed a decrease in their concentration, and there is an important concentration increase in the elements listed between Si and K. There is no significant variation in Ca contents during this retention period.

On the other hand, an enrichment factor F can be defined,

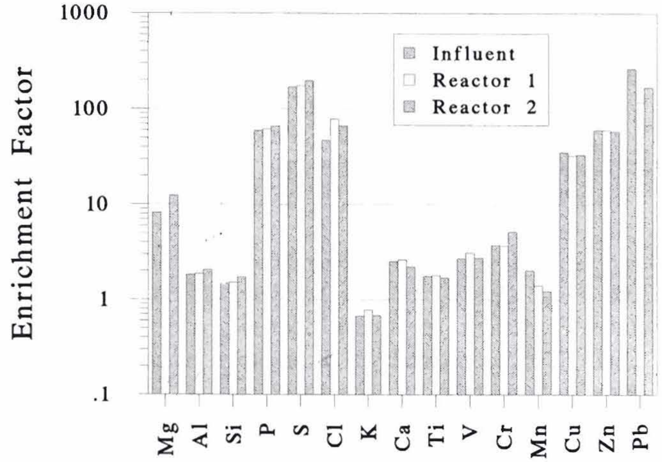

Figure 5. Average enrichment factors relative to Fe, for all elements measured in the sludge

for the elemental concentrations based on the average Earth crust composition, by the equation:

$$F = \left(\frac{C_Z}{C_{Fe}}\right)_M \left(\frac{C_Z}{C_{Fe}}\right)_{EC}^{-1} \tag{3}$$

where C_Z is the concentration of element Z, C_{Fe} is the concentration of Fe, and the subscripts S and EC refer to the sample and the Earth crust, respectively. Average elemental concentrations in the Earth crust are available in many published data compilations (CRC 1993).

Figure 5 shows the average enrichment factors F for all the elements measured, and it is possible to see that elements P, S, Cl, Cu, Zn, and Pb tend to group as a serie with high enrichment factors as compared to the remaining elements. The latter elements can be considered as normal, if F is smaller than 10, that is, their concentrations are not much higher than the average concentration in the Earth crust. The high enrichment for several elements is in agreement with the fact that the wastewater carries detergents (P), is subjeted to a bacteriological treatment to be purifed (Cl), is subject to acid rain (S) and runs througth the pipelines in the MCMZ that are mostly metallic (Cu, Zn, and Pb).

Table III shows that the permanence time in the digestors increases the enrichment factor for Al, Si, S, Cl, and K, and decreases for Ca and Cu. It can be said that only Cu suffers a decontamination process. Moreover, there is no significant change in the enrichment factor for V, Cr, and Zn .

CONCLUSIONS

The curves in **figures 2** and **3** demonstrate the consistency on the PIXE analysis performed in this work. On the other hand, the statistical method used shows the effect of the residence time in the digestors on the elemental concentrations. Thus, the methods employed here migth be an important criterion for the future digestors design.

The values on **table I**, together with the elemental concentrations found in the work by Malina and Pohland (1992), can be useful to calculate proportions in a mixture of soils and sludge highly enriched with some elements. For example, if the sludge analyzed in this work were combined in a ratio 30 to 1 with a soil with low P, S, Cl, Cu, Zn, and Pb contents, the result would be a soil with a very close concentration to the average composition.

The presence of P and S in the stabilized sludge suggests a possible use for agriculture, because these elements are a macronutrient and a secondary nutrient, respectively. However, the presence of toxic elements (Zn and Pb) should be kept in mind, as these elements prevent the use of soil for growing crops. It is important to point out that P has a limited availability in soils due to its low mobility and it must be periodically supplied through the application of fertilizers. Taking the concentrations for P in **table I** (around 8500 ppm) into account and the way it is assimilated by plants, the soil pH, the kind of phosphates (mono- or dibasic), the temperature, hydroxides, and organic matter, 10 ton of stabilized sludge would produce 10 ton of cotton per hectare (Rodríguez-Suppo 1989). The elemental characterization of sludge by PIXE permits their possible use as fertilizer or as a complement for the development of specific crops.

TABLE III. EFFECT OF RETENTION TIME IN A DIGESTOR COMPARED TO INITIAL ENRICHMENT FACTOR IN INFLUENT

		Change	
Element	**After 7 d**	**After 14 d**	**After 7-14 d**
Al		13 (20%)*	10 (14%)
Si		17 (12%)	14 (8%)
S		17 (20%)	
Cl	66 (6%)	42 (4%)	
K	16 (10%)		
Ca		-12 (6%)	-17 (2%)
Ti			-6 (6%)
V		0 (6%)	
Cr	0 (4%)		
Cu	-7 (20%)		
Zn	0 (10%)		

*Maximum error for statistical test in parenthesis

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