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 carries 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 $3.60 \times 10^9$ m³ a year of wastewater, which in turn generated $8.85 \times 10^9$ 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 digesters, 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 10³, 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 sedimentoed 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 digester (Soler et al. 1992). 20 of the 40 sedimentoed sludge samples, were processed in the same digester 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/cm² was obtained.

**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 Fisica, 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.
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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:

$$c = \frac{N_X}{S D}$$  \hspace{1cm} (1)

where $N_X$ (number of counts) is the peak area corresponding to a specific element, $S$ (number of counts per $\mu$C per g/cm$^2$) is the detection sensitivity for that particular element, $Q$ (in $\mu$C) is the total accumulated proton charge, and $D$ is the areal mass density of the sample (in $\mu$g/cm$^2$).

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/cm$^2$ 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 1 shows the elemental concentrations found in the

<table>
<thead>
<tr>
<th>Influent</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cl</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
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<td>AVG*</td>
<td>34400</td>
<td>21900</td>
<td>60500</td>
<td>8600</td>
<td>6000</td>
<td>890</td>
<td>2020</td>
<td>14600</td>
<td>1460</td>
<td>61</td>
<td>73</td>
<td>310</td>
<td>8360</td>
<td>290</td>
<td>590</td>
<td>370</td>
</tr>
<tr>
<td>STD*</td>
<td>24300</td>
<td>11100</td>
<td>29700</td>
<td>4300</td>
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<td>550</td>
<td>990</td>
<td>6700</td>
<td>710</td>
<td>13</td>
<td>33</td>
<td>550</td>
<td>4240</td>
<td>130</td>
<td>260</td>
<td>170</td>
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<tr>
<td>N*</td>
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<td>28</td>
<td>29</td>
<td>29</td>
<td>29</td>
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<td>29</td>
<td>26</td>
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</tr>
<tr>
<td>Reactor 1</td>
<td>AVG</td>
<td>24500</td>
<td>67600</td>
<td>9000</td>
<td>7100</td>
<td>1500</td>
<td>2500</td>
<td>17200</td>
<td>1600</td>
<td>66</td>
<td>48</td>
<td>200</td>
<td>9000</td>
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<td>29700</td>
<td>5300</td>
<td>3000</td>
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<td>1300</td>
<td>9100</td>
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<td>28</td>
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<td>25900</td>
<td>73600</td>
<td>9800</td>
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<td>13</td>
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<td>3</td>
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<td>Pr(x)</td>
<td>Inf-R1</td>
<td>0.18</td>
<td>0.18</td>
<td>0.14</td>
<td>0.09</td>
<td>0.02</td>
<td>0.04</td>
<td>0.11</td>
<td>0.21</td>
<td>0.37</td>
<td>0.92</td>
<td>0.85</td>
<td>0.27</td>
<td>0.63</td>
<td>0.17</td>
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<tr>
<td></td>
<td>Inf-R2</td>
<td>0.34</td>
<td>0.14</td>
<td>0.10</td>
<td>0.18</td>
<td>0.10</td>
<td>0.06</td>
<td>0.19</td>
<td>0.46</td>
<td>0.22</td>
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<td>0.71</td>
<td>0.23</td>
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<td>0.23</td>
</tr>
<tr>
<td></td>
<td>R1-R2</td>
<td>0.34</td>
<td>0.27</td>
<td>0.53</td>
<td>0.41</td>
<td>0.78</td>
<td>0.71</td>
<td>0.79</td>
<td>0.43</td>
<td>0.84</td>
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<td>0.32</td>
<td>0.39</td>
<td>0.42</td>
<td>0.50</td>
<td>0.64</td>
</tr>
</tbody>
</table>

*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 matrix, by energy loss calculations we obtain 28 μm range for 1.8 MeV protons in this target. Due to their origin, wastewater pollutants 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$_2$, MgSO$_4$.6H$_2$O, MgSO$_4$.Al$_4$(SO$_4$)$_3$.y Ca$_3$Mg(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/cm$^3$ for the mean target density, which made it possible to estimate a target thickness of $x = \sim 4$ μm (where, $x_0 = 1.12$ mg/cm$^2$). 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 $H_0: \mu_j = \mu_i$. $t$ 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 (eq. 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:

$$F = \left( \frac{C_z}{C_{Fe}} \right)_M \left( \frac{C_z}{C_{Fe}} \right)^{-1}_EC$$

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 series 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 subjected to a bacteriological treatment to be purified (Cl), is subject to acid rain (S) and runs through the pipelines in the MCMZ that are mostly metallic (Cu, Zn, and Pb).

Table III shows that the permanence time in the digesters 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 digesters on the elemental concentrations. Thus, the methods employed here might be an important criterion for the future digesters 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 (Rodriguez-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.

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