

ON THE USE OF AGRICULTURAL LITTER AS METAL ABSORBER

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ABSTRACT

Sugar cane bagasse resulting from the sugar cane alcohol industry was submitted to anaerobic fermentation. The resulting material was tested for its ability to remove uranium and zinc from natural waters. The enrichment factor observed was of the order of 10^4 and 10^3 , respectively, and the relaxation time about one hour when using lg of absorber material per liter of solution.

INTRODUCTION

The intensive industrial activity of the last decades has imposed important questions to modern society. One of the questions concerns degradation of the environment and the costs involved in the recovery of polluted natural systems. Mainly in developing countries the immediate benefits of industrial development are given priority when compared to environment preservation. The other question concerns the finite natural resources and the necessity of recycling or looking for other reserves less explored up to now (the ocean, for example).

The extraction of metals dissolved in waters both from the point of view of environment protection and exploration of new sources of raw materials finds its bottleneck in the costs and suitability of methods and substrates used in the extractive operations.

The classical methods of waste treatment, for example, are not specific for the extraction of heavy metals^{4,12,13}.

The physical-chemical form of the metals in solution will determine the procedure for extraction. Metals complexed to organics can not be coagulated and precipitated by chemicals without previous oxidation. This is necessary in order to liberate the ions otherwise unavailable for reaction. The adsorption on activated charcoal or on synthetic resins is more specific and can be efficient in direct applications, but the operation costs are high as are those of non-conventional methods based on electrolytic flotation⁷ and adsorption on special substrates^{1-3,5,8,9}. The recovery of economically interesting metals from natural matrices requires extensive stages of extraction and concentration due to the high degree of dispersion. The costs of such operations can be reduced when unexpensive material of high extractive capacity becomes available.

Wagener and Heitkamp¹¹ performed studies on the use of peat as an absorber for uranium extraction from sea water. These organic materials can work as strong absorbing agents either for metallic ions or for organometallic compounds, and they present kinetic advantages compared to titanium oxide and synthetic resins.

In the present work the objective was to make use of abundant agricultural litter, sugar cane bagasse, in order to produce an unexpensive material with properties required for extracting metals from natural waters and industrial waste. The absorbing capacity and kinetics of the material were tested using uranium (UO^{2+}) and zinc as model cations due to their respectively high and moderate preference for oxygen as the donor atom¹⁰.

The bagasse was submitted to fermentation in order to give development to ligand groups (carboxylic, aldehydes, alcoholic, phenolic, etc.).

EXPERIMENTAL

The absorbing material was prepared first by grinding the sugar cane bagasse as it was delivered from the alcohol industry. In order to check for the best fermentation procedure, two types of digestion were performed: one at 35° and other at 52°C. After the digestion, the material was dried at 60°C and again ground to a powder of density slightly higher than that of water.

The acidity index of this material was determined by titration with 0,01 N NaOH in a closed vessel to avoid interference of atmospheric CO_2 .

The tests for the capacity and kinetics of absorption were performed by exposing 1-5 grams of material to a known volume (5-10 l) of solution at 25°C and under constant agitation. The uranium extraction was tested using fresh seawater collected in polyethylene bottles previously conditioned with seawater. In the case of zinc, the absorption tests were made with a solution initially containing 5 ppm of zinc as zinc nitrate, and 2 g of sodium acetate per kg of solution. In both tests a polyethylene container pre-treated with calcium chloride solution was used as reactor vessel.

The initial concentration of both metals was always measured after 15 min. of contact between the test solution and the reactor walls under strong agitation. The concentra-

tion of metals in the absorbing material was also determined after the desired time of contact with the test solution.

Uranium was analysed spectrophotometrically using arsenazo III⁶ and zinc was measured by differential pulse polarography at pH 4.7.

RESULTS AND DISCUSSION

In general, the absorption on the produced material can be compared to an ionic exchange process where protons are liberated into solution. The acidity index of the absorber prepared from sugar cane bagasse was determined to be 0.70 ± 0.05 meq/g independently of the digestion temperature. This number characterizes the exchange capacity of the material. Synthetic resins have 3-4 meq/g.

To interpret the obtained data, an enrichment factor (Q) was used:

$$Q = \frac{g_{MA}/g_a}{g_{MW}/g_w}$$

where g_{MA} and g_{MW} are the amounts of metal in the absorber and in the water phase respectively; g_a and g_w are the amounts of absorber and of solution. Q can be determined measuring the cationic concentrations in solution before and after the contact with the absorber. Using the ratio of 1:1000 for adsorber (dry) vs. water, e.g. 1g per liter, Table 1 gives the percentage of metal bound to the absorber as function of the enrichment factor.

Table 1. Percent of originally dissolved metal which is finally bound to the absorber, as function of the enrichment factor.

Valid for a ratio of 1:1000 for absorber/water.

Separation factor Q	% of metal bound
100	9
500	33
1.000	50
5.000	83
10.000	91

The kinetics of absorption, independently of the fixation process, can be characterized by a relaxation time (τ) as given below:

$$\frac{Q_t}{Q_\infty} = 1 - e^{-t/\tau}$$

where Q_∞ is the maximum enrichment factor and t is the time of contact.

The curves of figures 1 and 2 show the results obtained for the absorption of uranium and zinc. In figure 1 the enrichment factor (Q), was plotted as function of pH.

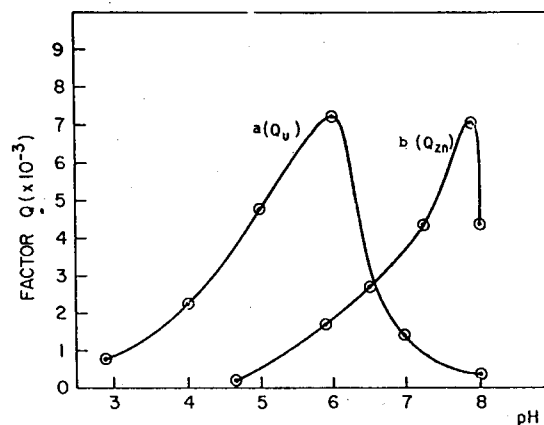


Figure 1. Variation of the enrichment factor Q as a function of pH, curves a and b stand for uranium and zinc respectively.

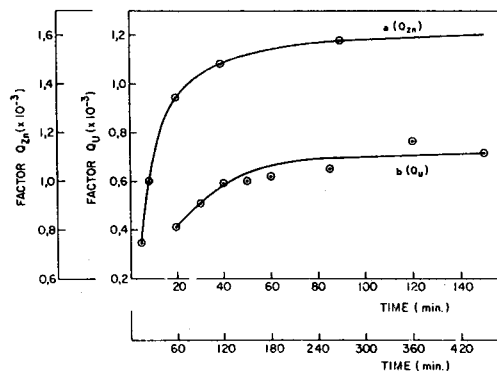


Figure 2. Dependence of the enrichment factor for zinc (curve a) and uranium (curve b) on the time of contact between solution and absorber.

In the case of uranium, the strong uranyl carbonate complex ($\beta = 10^{18}$) competes successfully with the absorber at pH > 6.5 in seawater.

The natural acidity of the absorber lowers the pH of seawater from 8.35 to 6.90 when 2g absorber/1 are used, but in the presence of carbonate ions the enrichment factor does not exceed 10^3 . At pH < 5 the competition between uranium and hydrogen ions decreases the absorbing capacity.

The interference of ions such as calcium and magnesium, very abundant in seawater, was tested and concentrations as high as 0.05 M (Mg) and 0.1 M (Ca) decreased the value of Q by a factor of only two.

The enrichment factor for uranium in seawater was equal to 2×10^4 at pH = 6 and is correlated to a relaxation time of 60 min.

Curve b from figure 1 shows the variation of Q relative to pH in the case of zinc absorption. The process of zinc absorption is limited to a range of pH between 4.5 and 8.0. At pH < 4.5 the hydrogen ion competes for the absorption sites and at values > 8.0 the active substances on the solid are solubilized.

The maximum enrichment factor for zinc was 1.6×10^3 at pH 6.4 and the relaxation time characterizing the rate of absorption was of 60 min.

CONCLUSIONS

The use of the absorber described here for extraction of uranium from seawater is limited by the competition with carbonate ions. The necessary reduction to 6 of the natural seawater pH can be attained using higher proportion of absorber to solution. After one hour of batch contact the concentration of uranium in the absorber can reach 2 to 3 ppm (concentration in seawater - 2 ppb).

Although the enrichment factor encountered for zinc is smaller than that for uranium in the absence of carbonate, it still shows that after one hour of contact the concentration of metal in the aqueous phase is reduced by 90% when using 1g of absorber per liter of solution ($Q = 10^4$).

Preliminary results for the extraction of cadmium showed a reduction of 94% in the metal concentration initially in solution for the same proportions absorber/solution given above.

The greatest advantage of the absorber obtained from sugar cane bagasse, besides the low costs, is the fast kinetics of exchange. Materials like titanium oxide and synthetic resins require 100-500 hours of contact to reach the enrichment factors obtained here after 60 min. This fast kinetics was also encountered by Wagener and Heitkamp¹¹ when working with humic material as metal absorber.

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ARTIGO

COMPOSTOS DE COORDENAÇÃO ENTRE OS HEXAFLUOROFOSFATOS DE LANTANÍDEOS (III) E O TRIMETILFOSFATO

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ABSTRACT

This present work is concerned with the synthesis and characterization of the compounds obtained from the reaction of hexafluorophosphate of lanthanides (III) and trimethylphosphate (TMP). The analytical results and conductance measurements indicated the composition $[\text{Ln}(\text{TMP})_7](\text{PF}_6)_3$.

These compounds were characterized by elementary analysis, molar conductance, melting point, vibrational spectra and potentiometric titration.

The infrared spectra showed that the ligands coordinated to metal through the phosphoryl group oxygen as well as indicated that PF_6^- is not coordinated.

INTRODUÇÃO

Em 1965 iniciaram-se os estudos de compostos formados entre o trimetilfosfato (TMP) e sais metálicos. Teichmann e Hillegat¹ isolaram compostos halogenados de Fe (III) e Ti (IV) com este ligante, na proporção metal/ligante de 1:2 e 1:3. Gutmann e Leitmann² sintetizaram compostos de fórmulas: $\text{M}(\text{ClO}_4)_2 \cdot 6\text{TMP}$, $\text{M} = \text{Co}, \text{Ni}$ e Cu e $\text{V}(\text{ClO}_4)_2 \cdot 5\text{TMP}$. Em 1970, Graham e Joesten³ prepararam e caracterizaram compostos do trimetilfosfato com percloratos de lantanídeos (III) e uranila. Os compostos obedeceram as seguintes formulações químicas:

a) $\text{Ln}(\text{ClO}_4)_3 \cdot 7\text{TMP} \cdot n\text{X}$ ($\text{Ln} = \text{La}, \text{Tb}$ e Er ; $\text{X} = \text{H}_2\text{O}$ e