HUMIC SUBSTANCES APPLIED TO THE PURIFICATION OF THE WASTEWATER FROM INGA BRAZILIAN ZINC COMPANY

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I. INTRODUCTION

Wastes containing large amount of heavy metals, such as those from mining and metallurgical activities, present a big problem for sustainable development. Heavy metals are not degradable and can only be scattered in the environment when showing a low biogeochemical activity form. Behavior of metals in the environment depends in many ways upon their migration forms and the subsequence influence on the total metal concentration in the ecosystem. In order to understand migration processes and analyze the toxicity of heavy metals it is not enough to determine only their gross content. It is also necessary to differ the forms of metals content as it is dependent on their chemical and physical structure, being the most dangerous the labile forms, which are of high biogeochemical activity.

Therefore, the detoxification of wastes as well as the contaminated soil and water containing high concentrations of heavy metals consist in an important and actual environmental problem and are, consequently, due to concern.

Many companies and scientific groups around the world have been investigating possible routes for the treatment of such wastes. The Russian company EPhAT Ltd. has reasonable experience in the development, adoption and successful use of effective detoxification technologies of industrial and urban waste, purification of wastewaters, re-cultivation of infracted, degraded and polluted soils and sub soils, based on the usage of humic substances. The EPhAT Company produces a number of different formulations of humic substances from mineral coal. The EphAT humic mineral concentrates (HMC) have distinctive physico-chemical characteristics for different applications.

In natural waters, zinc will mainly be present as the cation Zn^{++} but complexes with carbonates and hydroxide may also be found. The participation of organic complexes is still not well described (Gron and Andersen, 2003). Humic substances are present in all soils and natural waters and are believed to be products of transformations of organic residues and animals promoted by soil microorganisms. In addition to that, these substances are generally seen as an important component in soil and fresh water. Their role as the responsible component for the binding of the major part of the available metal ions is recognized, especially since its ability to act as a chelating agent is well documented. The particular effect that humic substances have on chelatable metals in wastes is dependant of a series of factors, which must be taken into consideration. Those factors are associated to the particular nature of the humic substance, the chemistry of the soil or water environment in question in terms of acidity-alkalinity and oxidation-reduction, as well as to the presence of competing species. In the specific case of the HMC, it has been observed that it can be effective by binding heavy metal ions and then turning them into water insoluble compounds. The mobility of metals ions is, as a consequence, sharply reduced, when not cleared out completely, and their migration to the environment is either significantly reduced or totally excluded (Stewart, 2002).

Environmental scientists have been showing interest in humic substances for a long time. This interest arose due to these substances interactions with soil and water pollutants and the consequent results on water and wastewater treatment processes.

Nevertheless there are still not many reports on the applications of humic substances in environmental remediation. Only some researches on the utilization of humates in the removal of metals from water or immobilization of heavy metals in soil have already been reported (Kochany and Smith, 2001; Shulgin et al, 1996).

In this context, the evaluation of the use of three different types of HMC, produced by EPhAT. Ltd., in the Zn purification of the INGA wastewater, is the main focus of the present work.

II. MATERIAL AND METHODS

In the INGA company premises there is a wastewater reservoir containing a significant amount of zinc salts located adjacently to the waste dumps. This wastewater, as well as the waste dumps, are both sources of environmental pollution by heavy metals, such as cadmium, lead, copper, iron, nickel and manganese, and, more significantly, by zinc.

Wastewater samples utilized in the purification studies came from the original specimen taken from the INGA company reservoir which had a slight red color.

The analysis of this wastewater sample resulted in the following data: pH of 5.7 and zinc content of 5500 mg/L.

Samples of 20 mL were poured into previously prepared glass recipients of 50 mL capacity. The recipients were numbered from 0 to 6. The one numbered 0 corresponding to the control was not mixed with any type of HMC.

In possession of these recipients, a known dose of reagent was introduced into each recipient, well mixed and left to settle for 15 minutes. After sedimentation, the content of each recipient was filtered through “Blue Ribbon” paper filter and analyzed for zinc content on an atomic absorption spectrometer “Perkin-Elmer 603”.

EPhAT’s HMC types 1,2 and 3 were tested separately as reagents in dosages determined by previous experiences.

III. RESULTS AND DISCUSSIONS

Tests using HMC-1

After testing different dosages of HMC-1 for the purification of the wastewater in question, the optimal dose of reagent was found to be 3.09 g/L. In this case, the use of HMC-1 provided a reduction of the zinc content to 2400 g/L, being the purification effectiveness not higher than 54%. At the same time, after sedimentation and filtration the final water kept a yellow-brown color typical of these reagents. Several different dosages of HMC-1 were also tried, nevertheless the purification of this wastewater from zinc by the usage of this reagent did not seem to be efficient.

Tests using HMC-2

The results obtained from the use of HMC-2 as the purification reagent of the INGA wastewater were similar to the ones from the utilization of HMC-1. Therefore, regent HMC-2 also did not provide an efficient zinc removal treatment.

Tests using HMC-3

The using of HMC-3 provided, after sedimentation and filtration, clear and odorless final water.

Table 1 exhibits the results in terms of final zinc content for the treatment utilizing different amounts of HMC-3.

Table 1 - Results obtained by the use of HMC-3 for water purification

Specimen #		0	1	2	3	4	5	6
HMC-3 dose	mL/L	0	12.5	15	25	50	75	100
	%	0	1.25	1.5	2.5	5	7.5	10
	mg/L	0	6.25	7.5	12.5	25	37.5	50
Zinc Content	mg/L	5500	2620	4.8	23	34	30	38

It can be seen that the best result in terms of zinc removal was obtained in specimen number 2, when 15 mL/L of HMC-3 were used. In that specific case, the final zinc content was reduced to 4.8 mg/L, a value which represents less than 0.1% of the original value.

This fact can be explained by the formation mechanisms of the water insoluble zinc humate and zinc hydroxide in comparison to the water soluble zincates such as Na2[Zn(OH)4]. The optimum removal would occur for an optimum amount of HMC-3 where the insoluble compounds are preferentially formed and the solution pH did not interfere in their solubility, keeping them as such.

Table 2 shows the pH values observed in the treated wastewater after mixing with different HMC-3 amounts.

Table 2 - Final pH of wastewater while introducing different HMC-3 doses

Dose of HMC-3, mL/L	0	12.5	15	16	17.5	18.5	20	22.5	25
pH	5.7	6.5	7.4	8.3	9.4	10.5	11.4	11.5	11.6

It can be seen that the optimum zinc removal coincides with a treated solution having a pH very close to neutral (7.4), value where the formed zinc compounds should reach their lowest solubility.

IV. <u>CONCLUSIONS</u>

INGA wastewater presents a serious environmental problem and it has to be treated in terms of their heavy metal content such as zinc (5500 mg/L).

Of the three reagents tested, all of which provided by EPhAT Ltd., the one who proved to be the more effective while concerning the removal of zinc was HMC-3. By its use the zinc content of the wastewater was reduced from the initial 5500 mg/L to 4.8 mg/L at the dose of HMC-3 of 15 mL/L, 1.5 % of the volume of water or 7.5 mg/L as dry substance.

Based on the results presented in this paper and on the research group previous experience, it can be said that the HMC-3 is a promising reactant to treat the INGA wastewater. Besides the zinc purification, its use will possibly be efficient to the removal of other heavy metals since one can also consider the re-processing of the treated water solution.

The application of this method in large scale would not demand any expensive construction for physical-chemical purification facilities.

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