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POLYNOMIAL FITTING EMERGY EVALUATION OF THE BENEFITS EMPLOYED IN A TANNERY WASTEWATER TREATMENT PLANT

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ABSTRACT

The aim of this study was to evaluate the construction and operation of recycling plants in tanneries using emergy analysis. Tanneries wastewater presents different kinds and quantities of pollutants, provided by the variety of operational techniques used along the overall process. The operational conditions employed in this work correspond to an average tannery in Brazil. Two hypotheses were used for the evaluation of the wastewater treatment plant. The first considers recycling plants integrated with the tannery's processes and operations. In the second there are no recycling plants. With the use of emergy analysis, the amount of direct and indirect solar energy required in each wastewater treatment unit was determined. The present work exams the possible benefits generated by the recycling units. The triangular diagram tool was used to show the benefits. The use of emergetic ternary diagrams for environmental decision making to assist tanneries management is proposed. The solar emergy associated with the saved material (water, sodium sulfate, calcium hydroxide and chrome sulfate) by the recycling units (7.47E+17 sej/year) is higher than the solar emergy of the resources necessary for construction and operation of the recycling units (2.12E+17 sej/year).

1. INTRODUCTION

Most industry activities generate by-products with low degree of fit into the surrounding environment. This is usually called pollution. The characteristics and the amount of pollutants emissions are the result of technology and specific processes used in each industrial activity. Tanneries are responsible for great part of chemical pollution. Along their productive process, tanneries generate residues, which are mainly released to water, causing an excessive demand for oxygen, as well as an increase of toxicity levels.

The aim of this study is to exam and evaluate the implementation and operation of specific recycling units in a tannery, using emergy analysis.

Emergy is the available solar energy is used up, directly and indirectly, in transformations to make a product or service, measured in solar energy joules, sej [1]. By measuring both human and nature's work to generate products and services, the methodology places environmental and economic values on a common basis. The advantage of the emergy analysis lies on the possibility of comparing resources and services of completely different qualities (e.g. land, human labor and biodiversity).

The emergy analysis has been used to evaluate wastewater treatment systems [2-4]. In this work, emergetic triangular diagrams were used to show the benefits achieved from the implementation of the recycling units. The prompt visualization of the emergy accounting data makes possible to compare processes and systems with and without ecosystem services, to evaluate improvements and to follow the system performance over time. With emergetic triangular diagrams, aspects such as the interaction between systems and the interactions between systems and the environment can be readily recognized and evaluated [5, 6].

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2. METHOD

To assess the tannery wastewater, its residues and the possible treatment techniques it is necessary to identify the characteristics of the tannery that will be analyzed. Table 1 shows the characteristics of the tannery and the treatments analyzed [7].

Table 1. Characteristics of the tanning and waste treatment processes

Productive operational characteristics	
Leather production	25,000 kg/day
Final Product	Wet-blue
Work period	8 h/day
Water consumption (depilation and lime)	300%wt
Sodium sulfates consumption of lime bath	3% wt
Water consumption of tanning bath	100% wt
Chrome consumption	8% wt
Volume of effluent without recycling	750 m^3/day
Volume of effluent with recycling	675 m^3/day
Available area of the recycling system	Unlimited
Useful life of the wastewater treatment plant and recycling units	25 years

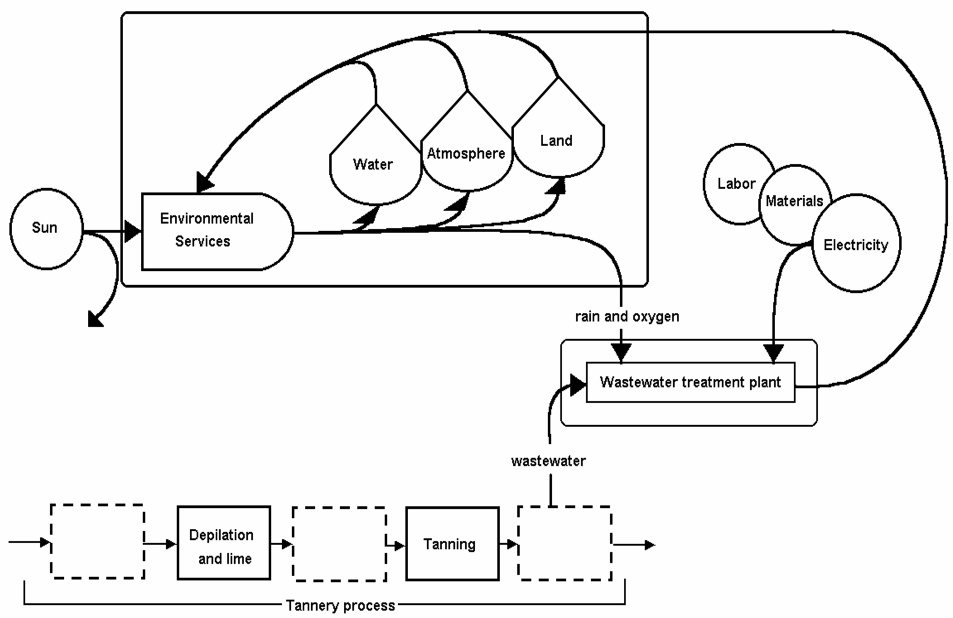

Figure 1. System diagram of wastewater treatment plant without lime and chrome recycling

The present study evaluates the treatment of wastewater in a tannery with:

1) No lime and chrome recycling (Fig.1);
2) Recycling systems of lime and chrome integrated with tannery's processes (Fig.2).

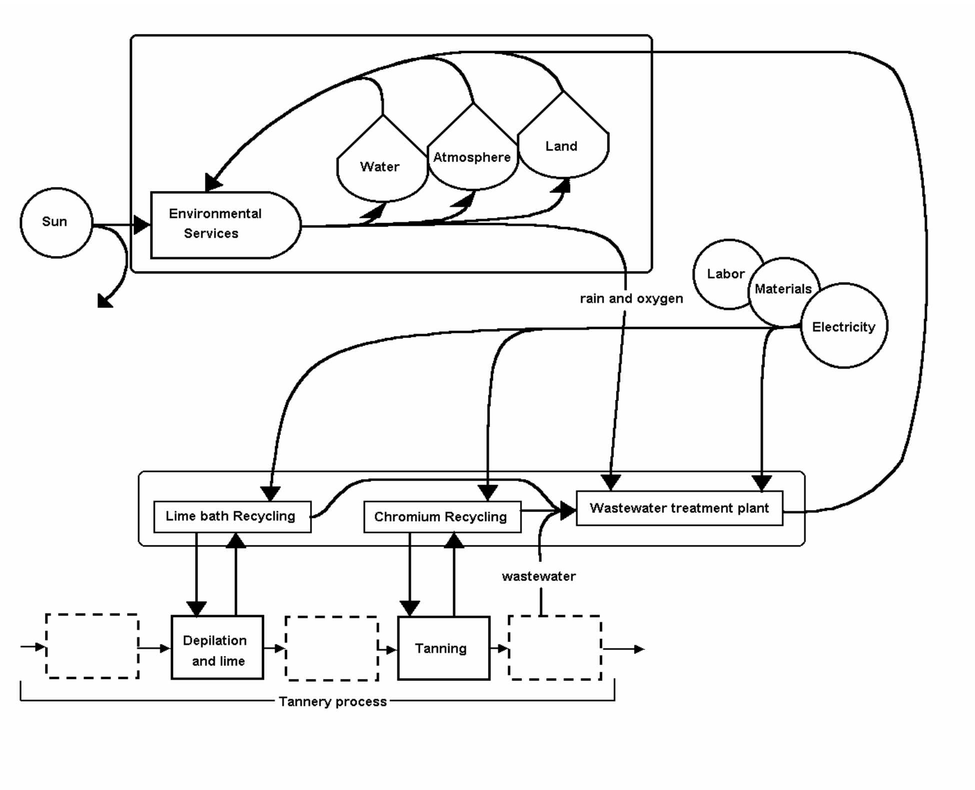

Figure 2. System diagram of wastewater treatment plant with lime and chrome recycling units

2.1. Description of the wastewater treatment plant

The wastewater treatment consists of a primary conventional treatment that comprises homogenization of wastewater with addition of coagulants and flocculants. For the secondary system (biological), mud activated by long aeration with characteristics similar to low-charge activated mud was adapted.

When dumped, the residual baths are driven to a self-cleaning sieve and to a pond for homogenization. This pond is provided with an aeration and shaking system for separation of solid material and sulfates oxidation. To this pond it is also added a solution of manganese sulfate for sulfur oxidation.

The flocculation pond receives solutions of aluminum sulfate and polyelectrolyte, which go to the primary decanter where the mud is separated from the wastewater. After that, the wastewater goes to the activated mud pond where oxidation of organic material occurs, and thereafter it is lead to the denitrification pond, to the aerobic reactor and finally to the secondary decanter where sludge and treated water are separated.

2.2. Preventive Treatment

In Brazilian tanneries, the recycling units are called preventive treatments, which target the reduction of sulfates in the lime, of the chrome salts in the tanning process and of the volume of water used in each process.

2.2.1. Lime Bath Recycling

The use of residual lime bath takes place after the removal of solid material, the volumetric correction of the baths, as well as the addition of the necessary sodium sulfate and lime.

The disposal from the lime baths goes to the collector and distributor pond. The baths are pumped to a sedimentation pond, followed by a storage pond for the partly recovered bath. By means of analytic control it is possible to determine the quantity of chemical products necessary to recover the original formulation. The recovered bath is used according to necessity. The sludge is sent to treatment without contact with other baths of the productive process.

2.2.2. Chrome Recycling

The chrome recycling consists in the precipitation of chromium as hydroxide after the tanning bath. After the precipitation process, chromium hydroxides are set aside from bath, re-dissolved in acid, and prepared for reutilization with adjusted basicity.

In the chrome recycling process the residual baths from tanning run, by gravity, to a collector and distributor pond. The baths are pumped to a sieve and disposed into a precipitation pond. An alkaline solution is added to this pond via dosage pump, which is ruled by potentiometer. The precipitate is then subjected to a press filter, and the resulting pies are treated with acid for dissolution and adjustment of basicity in appropriate ponds. This material returns to the tanning process. The filtered liquid runs to the main treatment homogenization pond.

2.3. Emergy Analysis

For the present study the energy diagrams of the tanning process without the lime and chrome recycling and with the recycling units are shown in Fig.1 and Fig.2 respectively. The emergy analysis tables were built, based on the energy diagrams. The annual amount of input and output of each flow was quantified in joules or grams. These amounts were multiplied by the respective amounts of direct and indirect solar energy used to obtain a joule or gram (transformity or specific emergy) of a given product or service. The transformities and specific emergies used in this study are shown in table 2.

Table 2. Transformities and specific emergy per unit used in this study

Item	**Solar emergy per unit**	**References**
Water	2.25E+05 sej/g	[10]
Rain	1.82E+04 sej/J	[3]
Copper	2.00E+09 sej/g	[11]
Concrete	7.34E+08 sej/g	[3]
Diesel	6.60E+04 sej/J	[1]
Electricity	1.65E+05 sej/J	[1]
Machinery	4.10E+09 sej/g	[12]
Oxygen	5.16E+07 sej/g	[9]
Plastic	1.50E+09 sej/g	[8]
Plastic in pipes	5.87E+09 sej/g	[1]
Chemicals	2.65E+09 sej/g	[1]
Human labor	7.38E+06 sej/J	[8]

Two types of benefits were identified: the benefits associated to the tanning processes, such as recovered material, Em(Rm), reduction of inputs, Em(Ri), and the benefits associated to wastewater treatment plant, such as reduction of inputs, Em(Rit) and the reduction of the environmental load by the reduction of oxygen consumption, Em(Ro). In this way, the total benefit can be assessed by Equation 1.

$$\text{Benefit} = Em(Rm) + Em(Ri) + Em(Rit) + Em(Ro) \quad (1)$$

2.4. Triangular Diagram

The emergetic triangular diagram [5, 6] is defined as a system of coordinates from an equilateral triangle whose height is equal to the unit. Each height is associated with one of the variables. Thus, any point in the triangle can be defined by three values of coordinates (for details, see the paper Graphical tool for emergy analysis: concepts and an example of application, C.M.V.B. Almeida, F. A. Barrella and B. F. Giannetti, in this volume).

For this study the coordinates are associated to the benefits, electricity and chemical products. As shown in Fig. 3a, the coordinate that extends from the base of the triangle to the upper apex was associated to the benefits, the coordinate on the right to the emergy of electricity and the coordinate on the left to the emergy of chemicals products.

In the emergy tables all the resources necessary to the units construction and operation were accounted. However, for analyses employing emergetic triangular diagrams we used the emergy of chemicals and electricity, which represent the main contribution to the total emergy of all systems analyzed. In the lime recycling unit electric energy accounts for 99 % sej/sej of the total emergy. In the chrome-recycling unit, chemicals account for 83 % sej/sej, while electricity 17 % sej/sej. In the wastewater treatment plant, the emergy of electricity and chemicals accounts for 97 % sej/sej of the total emergy.

The benefit coordinate is used to compare the emergy of investment in electricity and chemicals with benefits obtained (Equation 1). Fig. 3b shows the emergetic triangular diagram with the "drawn game" line. When a point is located on this line, it means that benefits are equal to the investments.

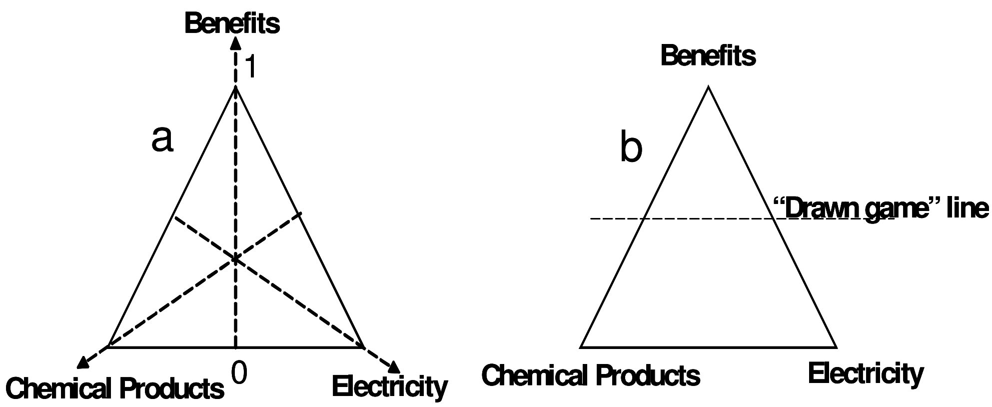

Figure 3. (a) System of coordinates of the triangular diagram and (b) Triangular Diagram with the "Drawn Game" Line

3. RESULTS AND DISCUSSION

3.1. Wastewater Treatment Plant without lime and chrome recycling units

In order to evaluate the benefits achieved by the implementation of recycling units, an emergy assessment was first performed for the wastewater treatment plant without recycling units (Table 3). For the account, the system construction and the plant operation were considered, obtaining the emergy necessary for the treatment of wastewater of 9.49E+19 sej/year. Concrete ponds, motors and pumps, electric wire, pipes, transportation of residues and human labor are the resources necessary for the construction of the wastewater treatment plant. With the account of all these resources we obtain the emergy necessary for the construction (3.82E+14 sej/year). For the plant operation, electricity, human labor, chemicals and rainfall were considered. Oxygen is a free renewable input from the environment needed for the aerobic oxidation of biodegradable organic material present in the effluent, and the sulfur present in the homogenization ponds. The oxygen emergy flow, as environmental free input, was also used by Brown and Ulgiati [8, 9] for fuels combustion in electricity production systems. Oxygen and rainfall are renewable resources, freely provided by the environment, and account for 3 % sej/sej of the total emergy necessary to the system (Table 3). The chemicals and the electricity are the resources with the major emergy in the system, accounting for 13 % sej/sej and 84 % sej/sej of the total emergy, respectively.

Table 3. Emergy evaluation of the wastewater treatment plant without recycling units

Note (*)	Item	Units	Type	Raw Unit/year	Emergy per unit sej/unit	Emergy sej/year
	Construction					
1	Ponds Concrete					
	Concrete	g	F	5.33E+04	7.34E+08	3.91E+13
2	Major equipment					
	Machinery	g	F	7.62E+04	4.10E+09	3.12E+14
3	Electric Wires					
	- Copper	g	F	7.66E-04	2.00E+09	1.53E+06
	- Plastic	g	F	2.83E-04	1.50E+09	4.25E+05
4	Plastic in pipes (PVC)	g	F	8.00E-03	5.87E+09	4.70E+07
5	Residues transport diesel	J	F	4.51E+08	6.60E+04	2.98E+13
6	Human Labor	J	F	1.67E+05	7.38E+06	1.24E+12
	Buildings (life 25 years)					**3.82E+14**
	Operation					
7	Oxygen	g	R	5.12E+08	5.16E+07	2.64E+16
8	Electricity	J	F	4.85E+12	1.65E+05	8.00E+17
9	Human Labor	J	F	4.79E+06	7.38E+06	3.53E+13
10	Chemicals					
	- Manganese Sulfate	g	F	6.83E+06	2.65E+09	1.81E+16
	- Aluminum Sulfate	g	F	3.90E+07	2.65E+09	1.03E+17
	- Polyelectrolyte	g	F	1.95E+05	2.65E+09	5.17E+14
11	Rainfall	J	R	6.08E+09	1.82E+04	1.11E+14
	Emergy for operation					**9.49E+17**
	Total Emergy					**9.49E+17**

(*) Detailed data and calculations may be obtained from the authors.

3.2. Lime recycling unit

Table 4 shows the emergy account for the lime-recycling unit. The emergy necessary for lime recycling is 6.61E+16 sej/year, including the recycling unit construction and operation.

Table 4. Emergy evaluation of lime recycling

Note (*)	Item	Units	Type	Unit/year	sej/unit	Emergy sej/year
	Construction					
1	Ponds (concrete)	g	F	3.90E+04	7.34E+08	2.86E+13
2	Machinery	g	F	1.40E+04	4.10E+09	5.74E+13
3	Electric Wires					
	- Copper	g	F	2.55E-04	2.00E+09	5.10E+05
	Plastic	g	F	9.44E-05	1.50E+09	1.42E+05
4	Plastic in pipes (PVC)	g	F	2.50E-03	5.87E+09	1.47E+07
5	Residues transport diesel	J	F	2.36E+07	6.60E+04	1.56E+12
6	Human Labor	J	F	5.58E+04	7.38E+06	4.12E+11
	Buildings (life 25 years)					**8.80E+13**
	Operation					
7	Electricity	J	F	4.00E+11	1.65E+05	6.60E+16
8	Human Labor	J	F	1.23E+06	7.38E+06	9.05E+12
	Emergy for operation					**6.60E+16**
	Total Emergy					**6.61E+16**

(*) Detailed data and calculations may be obtained from the authors

The emergy necessary for the construction of the lime recycling plant is 8.80E+13 sej/year. This value accounts for 0.2 % sej/sej of the total emergy for construction and operation. The operation of the lime recycling plant consumes only energy and human labor; the process doesn't require the use of purchase goods. For re-using the residual lime baths it's necessary to replace the contents of the composition of the initial bath. However, since this process is made in the depilation and lime, it's not a recycling unit cost. Table 5 shows the benefits obtained with the constructions of the lime recycling plant. The lime recycling leads to savings on water, sodium sulfate and calcium hydroxide, which once recovered are sent back to the depilation and lime process. The emergy of the benefits obtained by the lime recycling (4.16E+17 sej/year) is greater than the emergy necessary for the construction and operation of the recycling system (6.61E+16 sej/year).

Table 5. Benefits of the lime recycling unit

Note (*)	Item	Units	Raw Unit/year	Emergy per unit sej/unit	Emergy sej/year
	Recovered Material				
1	Water	g	1.29E+10	2.25E+05	2.89E+15
2	Sodium Sulfate	g	9.75E+07	2.65E+09	2.58E+17
3	Calcium Hydroxide	g	5.85E+07	2.65E+09	1.55E+17
	Total Emergy Benefits				**4.16E+17**

(*) Detailed data and calculations may be obtained from the authors

3.3. Chrome Recycling Unit

In this unit, as shown in table 6, the emergy needed for construction and operation is 1.46E+17 sej/year. The chemicals, sodium hydroxide and sulfuric acid, necessary for the plant operation account for 83% sej/sej of the total emergy. This input is necessary for chrome sulfate recovering.

Table 6. Emergy evaluation of chrome recycling

Note (*)	Item	Units	Type	Unit/year	sej/unit	Emergy sej/year
	Construction Phase					
1	Ponds Concrete					
	Concrete	g	F	1.25E+03	7.38E+08	9.18E+11
2	Glass (fiberglass)			1.50E+04	3.00E+09	4.50E+13
3	Machinery	g	F	3.45E+04	4.10E+09	1.41E+14
4	Electric Wires					
	- Copper	g	F	2.55E-04	2.00E+09	5.10E+05
	- Plastic	g	F	9.44E-05	1.50E+09	1.42E+05
5	Plastic in pipes (PVC)	g	F	2.50E-03	5.87E+09	1.47E+07
6	Residues transport diesel	J	F	5.15E+06	6.60E+04	3.40E+11
7	Human Labor	J	F	5.58E+04	7.38E+06	4.12E+11
	Buildings (25 years)					**1.88E+14**
	Operation Phase					
8	Electricity	J	F	1.51E+11	1.65E+05	2.49E+16
9	Human Labor	J	F	4.62E+05	7.38E+06	3.41E+12
10	Chemical Products					
	- Sodium Hydroxide	g	F	2.60E+07	2.65E+09	6.89E+16
	- Sulfuric Acid	g	F	1.95E+07	2.65E+09	5.17E+16
	Emergy for operation					**1.45E+17**
	Total Emergy					**1.46E+17**

(*) Detailed data and calculations may be obtained from the authors

Chrome recycling represents savings on chrome sulfate, with 3.31E+17 sej/year benefits, which can be seen on table 7. As it has been shown, the chemicals used in the chrome recycling account for 83% sej/sej of the total emergy in construction and operation. However, the benefits generated in the process are twice the emergy necessary for the construction and operation of the recycling system.

Table 7. Benefits of chrome recycling unit

Note (*)	Item	Units	Raw Unit/year	sej/unit	Emergy sej/year
	Reduction Material				
1	Chrome Sulfate	g	1.25E+08	2.65E+09	3.31E+17
	Total Emergy Benefits				**3.31E+17**

(*) Detailed data and calculations may be obtained from the authors

3.4. Wastewater Treatment Plant with Recycling Units

The lime and chrome recycling system can't be analyzed solely, as they are preventive treatments, but recycling plants reduce the wastewater that goes to final treatment. Table 8 shows the emergy account of the wastewater treatment system, considering that recycling is part of the process.

Table 8.Emergy evaluation the wastewater treatment plant with recycling units

Note (*)	Item	Units	Type	Raw Unit/year	Tr sej/unit	Emergy sej/year
	Construction Phase					**3.82E+14**
1	Ponds Concrete	g	F	5.33E+04	7.34E+08	3.91E+13
2	Machinery	g	F	7.62E+04	4.10E+09	3.12E+14
3	Electric Wires					
	- Copper	g	F	7.66E-04	2.00E+09	1.53E+06
	- Plastic	g		2.83E-04	1.50E+09	4.25E+05
4	Plastic in pipes (PVC)	g	F	8.00E-03	5.87E+09	4.70E+07
5	Residues transport diesel	J	F	4.51E+08	6.60E+04	2.98E+13
6	Human Labor	J	F	1.67E+05	7.38E+06	1.24E+12
	Operation Phase					**9.26E+17**
7	Oxygen	g	R	3.12E+08	5.16E+07	1.61E+16
8	Electricity	J	F	4.85E+12	1.65E+05	8.00E+17
9	Human Labor	J	F	4.79E+06	7.38E+06	3.53E+13
10	Chemicals					
	Manganese Sulfate	g	F	6.14E+06	2.65E+09	1.63E+16
	Aluminum Sulfate	g	F	3.51E+07	2.65E+09	9.30E+16
	Polyelectrolyte	g	F	1.76E+05	2.65E+09	4.65E+14
11	Rainfall	J	R	6.08E+09	1.82E+04	1.11E+14
	Total Emergy					**9.27E+17**

(*) Detailed data and calculations may be obtained from the authors

To find out the total emergy of the system with recycling we have to add up the emergies of the lime recycling (6.61E+16 sej/year), the emergy of the chrome recycling system (1.46E+16 sej/year) and the emergy of the wastewater treatment plant (9.12E+17 sej/year). The total emergy of the wastewater recycling and treatment is 1.14E+18 sej/year. For both wastewater treatment plants, with or without recycling, the emergies necessary for construction are the same, as the facilities considered fit both situations. Table 9 shows the benefits obtained in a wastewater treatment plant due to recycling processes in the tannery, chemicals are saved and there is a reduction of the oxygen consumption, leading to a benefit of 2.25E+16 sej/year. The benefits obtained in the wastewater treatment plant are not significant, but if added to the benefits associated to the tannery process as a whole, play an important role not only in diminishing the environmental load but also in reducing substantially the purchased inputs in both tanning and treatment processes.

Table 9. Benefits wastewater treatment plant with recycling units

Note (*)	Item	Units	Raw Unit/year	Tr sej/unit	Emergy sej/year
1	Reduction Material				
	- Manganese Sulfate	g	6.83E+05	2.65E+09	1.81E+15
	- Aluminum Sulfate	g	3.90E+06	2.65E+09	1.03E+16
	- Polyelectrolyte	g	1.95E+04	2.65E+09	5.17E+13
2	Environmental Load reduction				
	- Oxygen	g	2.00E+08	5.16E+07	1.03E+16
	Total Emergy Benefits				**2.25E+16**

(*) Detailed data and calculations may be obtained from the authors

3.5. Triangular Diagram

Fig. 4 shows the position of the recycling units in the triangular diagram. Point 1 represents the lime-recycling unit, with corresponding benefits. The emergy of electricity accounts for 99% sej/sej of the total emergy, but as it can be seen in the triangular diagram the benefits are beyond the “drawn game” line, totalizing 37% sej/sej.

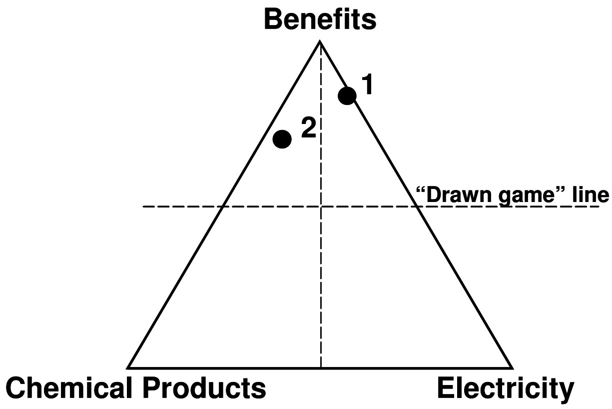

Figure 4. Triangular Diagram with recycling units: (1) Lime Recycling Unit; (2) Chrome Recycling Unit

In the chrome-recycling unit, chemicals have the greatest emergy value. Despite the large use of chemical inputs, the benefits are great, being above the “drawn game” line.

In Fig. 5 the triangular diagram of the wastewater treatment plant with and without the recycling units can be observed. Point 1, corresponding to the wastewater treatment plant without recycling units, shows that there are no benefits. Point 2 shows the benefits with recycling units in the tanning process, as well as in the wastewater treatment plant. The benefits don’t reach the “drawn game” line, but there are environmental benefits such as recovered material, Em(Rm), reduction of inputs, Em(Ri), reduction of inputs, Em(Rit) and the reduction of the environmental load by the reduction of oxygen consumption, Em(Ro). This is shown in the diagram by the shift of point 1 to point 2.

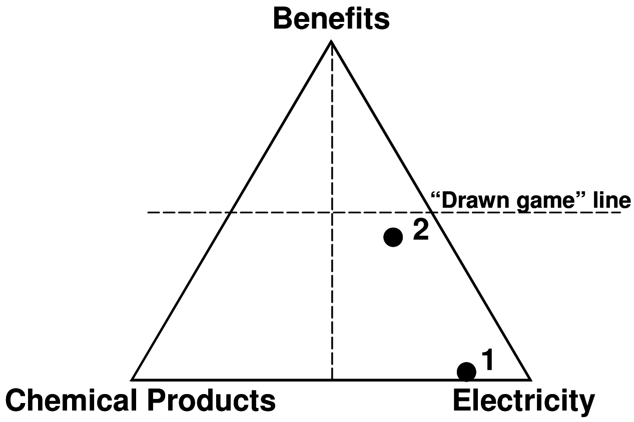

Figure 5. Triangular Diagram: (1) Wastewater treatment plant without recycling processes, (2) Wastewater treatment plant with recycling units

4. CONCLUSIONS

The outcome from the emergy analysis allows some conclusions:

1) The preventive treatment is a highly efficient process in pollution reduction. The solar emergy value of the material recovered and saved by the recycling units (7.47E+17 sej/year) is higher than the solar emergy of the resources necessary for construction and operation of the units (2.12E+17 sej/year).
2) To obtain chrome sulfate it's necessary the use of chemicals such as sodium hydroxide and sulfuric acid. The emergy of chrome sulfate (3.31E+17 sej/year) is greater than the emergy of the inputs used in the process (1.46E+17 sej/year).
3) The emergy analysis shows the benefits obtained by recycling plants to the environment, such as a reduction of 2.89E+15 sej/year in water use and 1.03E+16 sej/year in oxygen use. There is a greater environmental load in wastewater treatment without the recycling units, since the system will use more water and will need more oxygen for sulfur oxidation.
4) The triangular diagram can be used as a tool for environmental management, making possible the prompt view of emergy analysis results and the comparison between the systems. The "drawn game" line of the triangular diagram can be used as a tool for investment analysis, comparing benefits and investments.

Discussion inserted by the Workshop editor

"Recommendations for future work:

In this paper the process requires some oxygen that is accounted as a free emergy sources together with rain. That might be correct, but, since the process requires fossil fuels direct and indirect through labor and service, and is accounted for; the emergy for oxygen for the process under study is probably double counted. Oxygen is a co-product from the generation/transformation process of making fossil fuels/wood. Therefore when accounting for oil, diesel, wood or other carbon rich products, accounting for oxygen would be double counting of emergy? This question to be discussed in future scientific meetings."

Authors' considerations:

The authors do not agree that the use of oxygen as a free emergy source represents double counting. The time window that encloses the oxygen formation is other than that used for the emergy accounting in this study. Despite oxygen can be generated during petroleum formation; its genesis on earth is anterior to the oil formation. Oxygen levels reached their current levels about 400 million years ago, although some sources say this occurred 1.5 billion years ago. Most petroleum (58%) is produced from rocks of Cenozoic age (65,500,000 to the present), with 27% produced from rocks of Mesozoic age (251,600,000 to 65,500,000 years) and only 15% from rocks of Paleozoic age (542,000,000 to 251,000,000 years). On the other hand, two major coal-producing periods are known in geologic history, during the Carboniferous (359,200,000 to 299,000,000 years) and Permian Periods (299,000,000 to 251,000,000 years). If a time window including the oxygen formation were used, it would be also double counting the use of water or rain as emergy sources. Possibly everything in the universe is connected to everything else directly or indirectly, but we must concentrate our attention on a "window" in the scale of time and space. For a detailed discussion see reference [1], pages 96 and 97.

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