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Characterization of Industrial Highly Organic Wastewater to Evaluate Its Potential Use as Fertilizer in Irrigation of Agricultural Land

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1. Introduction

According to the United Nations [1], the worldwide consumption of water for industrial use represented 20% of the total available, equivalent to 784 km³year. The prediction is that by the year 2025, the consumption of water by industry will have increased by 50%. On the other hand, it is estimated that the wastewater produced by this sector generates around 500 million tonnes of organic matter per year [2], which should be treated adequately prior to its being released to water bodies.

On the other hand, agriculture is the productive sector with the greatest water consumption around the world, reaching 70% of the total annual withdrawal [3]. In several developing countries, approximately 95% of the extracted water is used for agricultural activities and therefore plays a key role in food production and food security [4].

The generation by the industry of wastewater with a high content of organic matter is considered a side-effect of some production processes. The treatment of such waters represents a cost, but also involves a loss of nutrients that are contained in these effluents or, when discharged without treatment to water bodies, they represent a very important source of ecological deterioration. On the other hand, agricultural production requires high volumes of water and fertilizer application to achieve optimal yields.

Therefore, the 'controlled' application on agricultural soils of industrial wastewater with a high content of organic matter intends to achieve the reuse of water and its contained nutrients. The goal is to reuse residual water that otherwise represents a cost and/or a potential environmental

threat to the environment, and to recycle nutrients, incorporating the contained organic matter that will be transformed to nutrients that are required by agricultural crops.

It is important to mention that the application of wastewaters on agricultural soils is a practice carried out since ancient times. However, their use may affect the integrity of the soil and groundwater when the organic matter application is larger than the degradation/assimilation capacity of the soil. Large amounts of organic matter and water on the soil for long periods will cause depletion of oxygen; therefore, the anaerobic decomposition of the organic matter could cause the generation of methane, the reduction or loss of agricultural production, and the potential groundwater pollution with elements such as heavy metals, salts, etc.

This work presents a model developed to correlate factors and relationships between soil-plant-wastewater and to evaluate the implications of the quality of the wastewater on the soil and plants, depending on their properties and nutrient requirements/thresholds. To evaluate the model some calculated test cases are discussed.

The model is based on the application of a set of mathematical equations, taken from different authors, to estimate the optimal conditions for the application of wastewater to the soil. Equations with more conservative results were considered, in order to avoid saturation of the soil and groundwater pollution.

2. Application mechanisms of wastewaters on agricultural soils

We found three different practices for the application of wastewaters with high organic matter content. The first one is the *slow-rate application*, which consists of the application of a controlled hydraulic load on soil covered with determined vegetation. The soil, through percolation, filtrates the components of the wastewaters. The second practice is the *fast infiltration*, which is used for wastewaters that have received any type of pre-treatment and are applied in large amounts on highly permeable soils, allowing the waters to get quickly to the aquifer in the correct amount. Finally, *surface irrigation*, which implies the distribution of wastewaters on the surface of soils with vegetation coverage, controlled slopes, and low permeability. The objective of this treatment is the filtration of water through the runoff of the vegetation coverage [5].

This study uses the slow-rate application criteria, carried out intermittently to allow for ground aeration. The period between applications makes easier the degradation of organic matter and the nutrients of the wastewaters to bioavailable forms for the plants. Otherwise, the lack of oxygen causes an anaerobic decomposition that affects the development of the plant [6]. The slow-rate application can be of two types:

Type I, which applies the *maximum hydraulic load*. This type provides large amounts of water to small land surfaces and is mainly used in humid regions. This application criterion depends on the soil permeability or on the nitrogen discharge. Additionally deep percolation and soil transpiration should be considered [7].

Type II searches for the *irrigation optimal potential*. In this type, the water treatment is the secondary objective and the minimum amount of water to maintain the crops is applied, according to their water and nutrient requirements. This criterion is usually applied in dry lands. [7]

This study considers the two types described above for land application of the wastewater. The application of slow-rate Type I is a mechanism of organic matter removal from wastewater, while Type II is used to determine the minimum water volume to be applied in order to fulfil the physiological requirements of the crop. It is very important to consider that the amount of applied wastewater does not pretend to cover totally the crop's requirements; it only represents an additional amount of water that will benefit the crop's development.

Characteristics that the soil must fulfil for the slow-rate application (Type I and II) are described in Table 1.

The land application of wastewaters is to be based on a limiting design parameter, which controls the application design and determines the size of the hydraulic load rate that can be managed. In order to determine the limiting design parameter (LDP), the following aspects must be considered: hydraulic capacity of the soil, nitrogen contained in the wastewaters, biochemical oxygen demand (BOD₅) of the wastewaters, and the amount of toxic elements such as heavy metals [7]. The LPD is defined based on the organic matter content of the wastewater, the soil permeability, or the nitrogen concentration of the wastewater.

PARAMETERS	SLOW-RATE CHARACTERISTICS
Climatic Restrictions	Requires storage facilities during the rainy or cold season.
Water Table Depth	0.6–0.9 m
Slope	<20% in ploughed land <40% in non-ploughed land (trees)
Soil Permeability	0.5–50 cm/h
Permeability Interval	0.15–50.8 m/h
Soil Depth	> 0.61 m

Table 1. Soil characteristics required for slow-rate application. [5,7]

2.1. Wastewater-soil-crop relation

The relation existing between the wastewater, soil, and crops is mainly based in the equilibrium of the constituents of each one of these elements. In such a way, the vegetative cycle of the crop depends on the amount of water and nutrients available for its development. This availability is related to the humidity retention capacity of the soil and its fertility, which depends, among other factors, on the amount of organic matter present in the soil and provided by the crops at the end of their vegetative cycle. The decomposition of the organic vegetal material, under adequate conditions, allows the liberation of nutrients that contribute to soil fertility [8].

VARIABLES		
Wastewater	Soil	Crop
Biochemical Oxygen Demand	Texture	Nitrogen Requirement
Total Suspended Solids	Structure	Phosphorus Requirement
Fat and Oil	Permeability	Potassium Requirement
Metals	Water Table Depth	Toxicity to Metals
Nitrogen	Organic Matter	Sensibility to Salinity
Phosphorus	pH	Sensibility to Boron
Potassium		Evapotranspiration
Boron		
Salinity		
Sodium Absorption Relation		
Nitrogen-Carbon Relation		

Table 2. Characteristics of the variables in the soil-crop-water relation. [5,9–10]

The evaluation of wastewaters presented in this study is based on the relation existing between the water, the soil, and the crops, where the used water is an effluent of the alimentary and beverage industries. Therefore, the wastewaters present high contents of organic matter, suspended solids, and nutrients that modify these relations, affecting the soil, the crops, and the groundwater. The most relevant characteristics of the wastewaters, due to their potential effect on the previously described relations, are the concentration of Biochemical Oxygen Demand, total nitrogen, heavy metals, salinity, and boron.

The proper operation of the proposed application must control the main characteristics of each one of the variables of the relation, maintaining a balance between them. Table 2 lists the characteristics considered in the present application.

2.2. Removal mechanisms of the wastewater constituents

The present research uses the soil as the degradation/filtrating medium of the organic matter contained in the wastewater and the model is based on the diverse mechanisms, which are performed by the soil and the plant, for the removal of the constituents of the wastewater.

Bacteria, actinomycetes, and fungi, which are found in large amounts on the superficial layer of the soil, carry out the elimination of the BOD₅ from the applied wastewater. Once the organic matter has been degraded, some components become available as nutrients for the crops [7].

The removal mechanism of the BOD₅ depends on the application period, the drainage of wastewater, and the aeration period of the soil. The limits of the load that can be supplied to the soil must be based on the maintenance of the aerobic conditions of it, for which it is necessary to have an aeration period longer than the BOD₅ application time [11].

Consequently, the application must take into consideration that the BOD_5 of the applied organic matter is to be smaller than the amount of oxygen present in the soil.

The removal of nitrogen is complex due to the way this element is typically found in industrial wastewaters, such as: N_2 , organic N, NH_3 , NH_4 , NO_2 , and NO_3 . [5] The manual for the design of soil wastewater treatment process of the US EPA [12] explains that the more oxidized the nitrogen form is, the more effective its retention and removal can be.

The nitrogen uptake of the crop is the main removal mechanism in the low-load application. However, denitrification and volatilization can be important depending on the wastewater constituents and the application place, according to the weather conditions.

There are different removal mechanisms of this element depending on the way it presents in the wastewater. The organic nitrogen can be trapped or filtrated by the soil; the ammonium (NH_4) and the ammonia (NH_3) can be volatilized, captured by the plant, or absorbed by the soil; and the nitrates (NO_3) can be absorbed by the plant or denitrified and liberated to the atmosphere in molecular nitrogen form [11].

The immobilization and storage of the nitrogen depends directly on the relation carbon/nitrogen (C/N), which determines the time in which the nitrogen is mineralized becoming available for the plant. Therefore, the optimum relation in the wastewaters for the application should be between 20:1 and 30:1 [13].

The metal removal of the wastewaters, according to [7], is given by the absorption of the soil, precipitation, ionic exchange, and complexation. The silt/clay or fine texture soils allow for almost complete removal of metals. In such a manner, plants have the capacity of removing metals from wastewaters by means of the evapotranspiration process that liberates the water from the environment and confines the metals in their structure. Consequently, these plants should not be used for feeding purposes. It is important to mention that for this research, the use of wastewaters with heavy metals is restricted.

The removal of phosphorus must take into account the fact that its presence in wastewaters is extensive. Even though risks to human health have not been reported, it is considered a risk to the quality of the water bodies due to its eutrophication potential. In the industrial wastewaters, phosphorus can be present as orthophosphate (PO_4)-3, polyphosphate, or organic phosphorus. Phosphates are immediately available for the use of the microorganisms existing in the soil but they are not present in the plant [6].

In the soil, the removal mechanism of the phosphorus depends on the chemical relations carried out through long periods; therefore, the continuous discharge of wastewaters with phosphorus will reduce the retention capacity of this element. However, according to [9], this capacity will not be exhausted. On the other hand, the phosphorus removal due to the plant intake is achieved in 20-25% of cases. In this case, it is necessary for the soils to contain iron and aluminium oxides and calcareous substances so the removal of this element increases proportionally to the clay content and the time of contact with the soil.

Sodium removal from the wastewaters is caused by the cationic exchange in the particles of the soil and is due to the crop's absorption of salts, which accumulates these elements in its structure,

depending on its tolerance to salinity [10]. Sodium is an element considered in this research because its frequent presence at a high-level in the wastewaters may cause a detrimental effect on the crops due to the salinity or alkalinity that it generates. The excess of sodium with respect to the magnesium and the calcium has an effect over the osmotic potential, which reduces the water absorbing capacity of the plant. It also affects the soil structure, preventing the clay from retaining the cations therefore modifying the hydraulic capacity of the soil profile [14].

Boron removal is carried out by the soil as long as iron and aluminium oxides are present in its composition. Boron is an essential micronutrient for plants, but it can be toxic at relatively low concentrations. For the application of wastewaters, it can be assumed that all the applied boron that is not assimilated by the plants will be leached to the groundwater. Therefore, this element is to be considered in the monitoring process (daily crop inspections) of the application, in order to prevent contamination of water bodies and plant toxicity [9].

2.3. Characteristics of the soil and its role in the application of wastewaters

The physical, chemical, and biological characteristics of the soil determine the behaviour of the water in the soil. Therefore, in this part of the document, each of the characteristics of the soil will be described, as well as their influence on the application of wastewaters.

The texture refers to the size of the particles that form the soil, such as: clay, silt, and clay-silt. In the context of the application of wastewaters with a high content of organic matter, the size of the particle will influence the filtration and percolation capacity of the soil. Consequently, fine textures present a slow-infiltration and percolation, optimal for superficial irrigation; medium textures adapt better to low load rate application; and coarse textures allow for the application of the process of fast infiltration [6].

The structure represents the shape and degree of the particle aggregation, determining the water and air movement, and the porosity. The soil aggregates form pores, which allow for the conduction of air and water that defines the infiltration capacity of the soil [6].

The soil depth allows for the retention of the water particles depending on the time of their presence in the soil. This time depends on the application rate and the permeability of the soil. On the other hand, an adequate depth of soil allows the development of roots, microbial activity, and the separation between the wastewater and the saturated area [15].

The chemical properties of the soil influence the growth of the plant due to the nutrients' availability, the purification of wastewaters, and the hydraulic conductivity. The pH of the soil is a key variable that affects the physical, chemical, and biological properties of the soil. It is affected by different factors such as the precipitation rate, the irrigation water quality, the dissociation of the carbonic acid, the organic matter content, the weathering of minerals, the presence of polymers and aluminium hydroxide, and the application of nitrogenized fertilizers. Additionally, the pH of the soil has an influence on the solubility of different compounds, the activity of microorganisms in the soil, the crop's growth given the availability of nutrients and metals, the mobility of the chemical constituents of the soil, the clay dispersion, and the formation of aggregates. The application of wastewaters with a low pH for long periods may

affect the fertility of the soil and allow the leaching of metals. Most of the crops are properly developed in a pH range between 5.5 and 7.0 [16].

The buffering capacity of the soil is related to the amount of organic matter that is contained. This property prevents drastic fluctuations of the pH that may affect the plant and the microorganisms and, additionally, favours the capacity of cationic exchange [9].

The content of organic matter in the soil has an influence on the structure and provides energy to the microbial activity that allows for the formation of aggregates. A large amount of organic matter supposes a better structure and therefore a better water retention. On the other hand, the decomposition of organic matter forms humic substances that react with the clay particles (silicates), iron, and aluminium oxides forming bonds among the soil particles. This characteristic favours the capacity of cationic exchange since the nutrients are retained for the crops, as well as the metallic cations and the organic chemicals, due to the larger specific surface of the soil particles [16].

The amount of organic matter is related to the absorption and availability of nutrients (micronutrients) for the plant, allowing the formation and availability of stable compounds with polyvalent cations — such as Fe_3^+ , Cu_2^+ , Ca_2^+ , Mn_2^+ , y Zn_2^+ — reduces the metallic capitation by the crops and their mobility in the soil [9].

2.4. Objective of the crop in the application of wastewater

The role of the plant in wastewater application is to absorb the majority of the nutrients, depending on the type of crop, that are applied in order to convert them into biomass [12]. In this way, crops with larger nutritional requirements will extract larger amounts of nutrients, allowing the removal of larger amounts of them from the applied wastewater and to fitoremediate some contaminants, depending on associated bacteria at the roots.

In the application of wastewater at a low load rate, the role of the plants is mainly the removal of the nitrogen and in some cases the generation of a financial benefit by means of crop fertilization, preventing erosion, and increasing the infiltration rate. Usually, the wastewater does not have an appropriate C/N relation of the range between 20:1 and 30:1. However, the roots of the plants provide a source of organic carbon that helps with the process [6].

The evapotranspiration is the process that determines the amount of water that the crop requires for its physiological processes, considering the plant transpiration and the evaporation from the plant and ground surfaces. The amount of evapotranspiration depends on the atmospheric conditions: such as the solar radiation, air temperature, relative humidity, and the wind speed, as well as the water availability from the soil [11].

In summary, the present work is based on the interactions existing between the wastewater, soil, and crop — where the wastewater provides the nutrients in organic form during the percolation; the soil is the medium that is in charge of the removal, degradation, and storage of such nutrients; and the crop performs the extraction of the nutrients and their transformation into biomass. At the end of the process, the organic constituents of the percolated water are expected to be reduced, avoiding contamination of groundwater.

The success in the application of effluents with a high organic load onto the soil will depend on the correct interpretation of the phenomena that occur in the soil and its relation with the plant. For this reason, the computer model STAR ASA has been developed. This model uses a set of mathematical equations taken from different authors, that, when applied within a process, allow the estimation of the conditions to be considered when the wastewaters are applied to the soil, making the decision process easier. The selected models were selected from those that obtained positive results and the most conservative results, in order to avoid the saturation of the soil and the contamination of groundwater. The application of this model will provide the wastewater volume that can be applied to the soil, the required land surface for the application, the minimum necessary time between applications, and the amount of nutrients incorporated to the soil.

3. Selected mathematical models

The characterization of the wastewater presented in this study is based on the application of the STAR ASA model.

3.1. Water balance

In the low load application Type I, the water balance allows for the determination of the hydraulic load that has to be applied to the soil to at least fulfil the crop’s requirement, considering the part of water that percolates to the groundwater based on the permeability of the least permeable layer. Equation 1 shows the balance between the applied water (depth and precipitation) and use of water due to percolation and evapotranspiration [5, 9, 11]. Figure 1 shows a conceptual framework of this balance.

$$L_w = Et_c - Pr + P_w \tag{1}$$

L_w = Wastewater hydraulic loading rate — based on soil permeability [mm/d]

Et_c = Evapotranspiration rate [mm/d]

Pr = Precipitation rate [mm/d]

P_w = Design percolation rate [mm/d]

Figure 1. Water balance framework based on the soil permeability

L_n = Wastewater hydraulic loading rate — based on soil permeability [mm/d]

Et_c = Evapotranspiration rate [mm/d]

Pr = Precipitation rate [mm/d]

P_w = Design percolation rate [mm/d]

In the application of low load Type II, the water balance focuses on the better use of the irrigation water than in a water treatment system. However, it is considered in this study since it allows the determination of the minimum hydraulic load rate required by the crop for its optimal development. This model includes in the calculation the leaching requirement and the irrigation efficiency, which is defined as the capacity of irrigating a determined volume of water into a uniform land surface. Equation 2 [6,9] shows this balance, which can also be seen in the conceptual framework of Figure 2.

$$L_w = (Et_c - Pr) * \frac{(1 + LR)}{E_i} \quad (2)$$

L_w = Wastewater hydraulic loading [mm/d]

Et_c = Crop evapotranspiration [mm/d]

Pr = Precipitation rate [mm/d]

LR = Leaching requirement (fraction)

E_i = Distribution system efficiency (fraction)

Figure 2. Water balance framework based on irrigation

The leaching requirement is used in the application of low load Type II in order to estimate the amount of water to be added in addition to the crop's requirement, avoiding the accumulation of salts in the root area of the plant, therefore preventing adverse effects for the crop development. Equation 3 [10, 14] represents this calculation, with help of the electric conductivity of the applied wastewater and the electric conductivity that the soil can withstand without affecting its performance.

$$LR = \frac{CE_w}{5(CE_e) - CE_w} \quad (3)$$

LR = Leaching requirement (fraction)

CE_w = Average conductivity of irrigation water [dS/m]

CE_e = Required conductivity in drainage water to protect de crop [dS/m]

L_n = Wastewater hydraulic loading rate — based on soil permeability [mm/d]

Et_c = Evapotranspiration rate [mm/d]

Pr = Precipitation rate [mm/d]

LR = Leaching requirement (fraction)

3.2. Oxygen balance

As mentioned previously, the application of wastewater from the food and beverage industries implies the use of large concentrations of organic matter with a high BOD_5 . Consequently, it is important to estimate the amount of equivalent oxygen required for the oxidation of this organic matter by means of the microorganisms, maintaining aerobic conditions in the soil. It must be considered that the BOD_5 concentration does not show the Total Oxygen Demand (TOD) existing in the wastewaters. Therefore, Equation 4 [12] estimates the TOD by means of the addition of the BOD_5 and the concentration of the oxygen demand of the nitrogenous compounds (NOD):

$$TOD = BOD + NOD \quad (4)$$

TOD = Total oxygen demand [g/m³ ó mg/l]

BOD_5 = Biochemical oxygen demand [g/m³ ó mg/l]

NOD = Nitrogenous oxygen demand [g/m³ ó mg/l]

$$NOD = 4.56 \cdot \text{Nitrifiable Nitrogen} \quad (5)$$

The oxygen demand by the nitrogenized compounds is calculated from the wastewater nitrifiable nitrogen concentration [mg N-NH₃l] multiplied by an estequiometric coefficient equal to 4.56 mg of oxygen [12, 17].

3.3. Analysis of the diffusive transportation in the soil

In this study, the estimate of the soil oxygenation by means of the application of wastewaters with a load of organic matter is performed considering the diffusive transportation of the oxygen through the soil as the main source of oxygenation. To prove this supposition, it was necessary to use the analytic solution developed by Papendrick and Runkles [18], based on the second law of Fick (Equation 6). This solution allows the estimation of the concentration

of oxygen in the soil, at a given and determined depth and time, considering a constant respiration (Equation 7). The solution proposed by these authors was proven by Kanwar [19] and Prasanta [20], demonstrating that the flux of oxygen (mass O₂/area x time) is directly proportional to the gradient of oxygen concentration between the atmosphere and the soil, and with the microbial oxidation rate. Those researchers consider the microbial oxidation rate to be constant. However, in field conditions, the respiration rate increases with the fertility of the soil and consequently the flux of oxygen in the soil.

In this study, the estimate of the oxygenation of the land irrigated with wastewater with high loads of organic matter, considers the oxygen diffusive transport through the soil as the main source of oxygen, which is used by the model developed in [18] that calculates the concentration of oxygen in depth and time.

To calculate the required oxygen flow for soil aeration, an equation is used that considers the elapsed time, the diffusivity of oxygen in soil and the oxygen concentration in the atmosphere and soil [12, 17], through a balance between the amount of equivalent oxygen that requires the organic matter from wastewater and the time that must elapse to reach the oxygenation of the soil through diffusive transport.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \alpha \quad (6)$$

The initial and threshold conditions for the application of this model are:

$$\begin{aligned} C(x, 0) &= C_t \\ C(0, t) &= C_o \\ \delta C(t) / \delta x &= 0 \end{aligned}$$

Where:

$C(x, t)$ = Oxygen concentration at a given depth (x) and at a time (t) [cm³ O₂/cm³ air]

C_t = Initial concentration of oxygen in the ground [cm³ O₂ / cm³ air]

C_o = Concentration of oxygen in the atmosphere [cm³ O₂ / cm³ air]

t = Time [h]

D = Diffusivity of oxygen in the soil [cm² / h]

x = Depth [cm]

α = Edaphic respiration rate [h⁻¹]

The following solution is established:

$$C(x,t)= C_t - \alpha t + (C_o - C_t) * \operatorname{erfc} \frac{x}{2\sqrt{D * t}} + \alpha \left[\left(t + \frac{x^2}{2D} \right) \operatorname{erfc} \frac{x}{2\sqrt{D * t}} - x \sqrt{\frac{t}{\pi * D}} * e^{\frac{-(x^2)}{4D * t}} \right]$$

(7)

Where:

erfc = Complementary error function

In order to determine the oxygen flux in the soil, Equation 7 was applied with typical values of oxygen respiration and diffusivity (D). Table 4 shows three sets of values or tests used in the research.

	1st Test (P1)	2ª Test (P2)	3ª Test (P3)
Initial concentration of oxygen (Ct) (cm3 of O2/cm3 of air in the soil)	0.21	0.21	0.21
Respiration (α) (g of O2/m3 of air in the soil*d)	0.002125	0.0025	0.0125
Diffusivity of oxygen in the soil (D) (cm2 of soil / h)	259.2	89.1	89.1

Table 3. Typical values of oxygen respiration and diffusivity.

In each test, an equation with seven depth values (x) and six different aeration times (t) was applied. The relative concentrations of oxygen obtained in each case are shown in Table 4.

Relative Concentration of Oxygen (C/C0)							
	X (cm)	t = 0	t = 4	t = 8	t = 12	t = 16	t = 20
P1	0	1	1	1	1	1	1
	15	1	0.983	0.974	0.9673	0.20997	0.9566
	30	1	0.972	0.955	0.9421	0.20995	0.9210
	45	1	0.966	0.942	0.9231	0.20994	0.8922
	60	1	0.962	0.933	0.9090	0.20994	0.8691
	75	1	0.961	0.927	0.8990	0.20993	0.8510
	90	1	0.960	0.924	0.8919	0.20993	0.8369
P2	0	1	1	1	1	1	1
	15	1	0.970	0.953	0.9398	0.92853	0.9186
	30	1	0.958	0.927	0.9021	0.88051	0.8613
	45	1	0.954	0.914	0.8800	0.84983	0.8225

Relative Concentration of Oxygen (C/C0)						
X (cm)	t = 0	t = 4	t = 8	t = 12	t = 16	t = 20
60	1	0.953	0.908	0.8680	0.83124	0.7974
75	1	0.952	0.906	0.8619	0.82060	0.7818
90	1	0.952	0.905	0.8591	0.81486	0.7726
P3	0	1	1	1	1	1
	15	0.851	0.765	0.6990	0.64263	0.5928
	30	0.789	0.635	0.5103	0.40253	0.3063
	45	0.769	0.570	0.3999	0.24913	0.1125
	60	0.763	0.541	0.3398	0.15621	0
	75	0.762	0.530	0.3095	0.10302	0
	90	0.762	0.525	0.2954	0.07432	0

Table 4. Oxygen concentrations with values of α and D.

Once the relative concentrations of oxygen are calculated, the curves were drawn for each test, obtaining the polynomial equations based on the depth, as shown in Figures 3, 4, and 5.

Figure 3. Relative concentrations vs. depth, Test 1 (P1).

Figure 4. Relative concentrations vs. depth, Test 2 (P2).

Figure 5. Relative concentrations vs. depth, Test 3 (P3).

Using the previous diagrams, the polynomial equations that describe the profile of the oxygen concentration in the soil for each time step were obtained. The derivation of the polynomial, evaluated at $x=0$ (soil surface), presents the flux for each time. For a constant degradation, in a given period, the area under the curve flux vs. time will calculate the amount of consumed oxygen. In this way, the mass of oxygen represents the load of BOD that could be accepted per day. Table 6 shows the oxygen flux in the soil for each one of the performed tests.

Test 1		Test 2		Test 3	
9.6	cm ³ /cm ²	7.18	cm ³ /cm ²	27.068	cm ³ /cm ²
0.0096	L/cm ²	0.00718	L/cm ²	0.027068	L/cm ²
0.0004	mol/cm ²	0.00032036	mol/cm ²	0.00120775	mol/cm ²
136.5	g/m ²	102.5	g/m ²	386.5	g/m ²

Table 5. Oxygen flux estimated using typical values of respiration and diffusivity.

With these results, the flux of oxygen that the soil can receive, using typical values of respiration and diffusivity, was determined to be between 102.5 y 386.5 g/m². On the other hand, it was observed that the flux of oxygen in the soil is directly proportional to the increase of the edaphic respiration and depends on the coefficient of diffusivity of the soil. These two factors determine the increase of the gradient of the oxygen concentration of the soil, which increases the flux of oxygen.

Considering the obtained results, this research established the application of wastewater with oxygen requirements lower than 100g/m² as a maximum, avoiding soil anaerobic conditions.

3.4. Estimation of oxygen flux due to diffusive transportation

Once it is established that the aeration of the soil is produced mainly by diffusive transportation phenomena, the estimation of the oxygen flux using Equation 7 will require information of the edaphic respiration, which is only obtained by field experimentation; this constitutes a limitation for the application of this model.

For this reason, the estimation of the oxygen flux in this research will be performed considering a simplified diffusive model that will require no information related to the edaphic respiration but will allow the adequate estimation of a minimum level of oxygen flux in the soil.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (8)$$

In order to determine the oxygen flux in a simplified manner, this research selected the analytic solution of the Law of Fick (Equation 8), proposed in [17] — the determination of the oxygen flux considers the elapsed time, the oxygen diffusivity of the soil, and the concentration of

oxygen in the atmosphere and air in the soil, but it does not consider the edaphic respiration, as shown in Equation 9. This model establishes a minimum concentration of oxygen in the root area of the soil in order to avoid negative effects in the crop development.

$$N_{O_2} = 2(C_{O_2} - C_p) \sqrt{\frac{D_p \cdot t_a}{\pi}} \quad (9)$$

N_{O_2} = Flux of oxygen crossing the soil surface [g/m²]

C_{O_2} = Vapour phase O₂ concentration above the soil surface [g/m³ o mg/l]

C_p = Vapour phase O₂ concentration required in soil to prevent adverse yields or root growth [g/m³ o mg/l]

D_p = Effective diffusion coefficient [m²/d]

t_a = Aeration time

$$D_p = 0.66 \cdot \epsilon \cdot S \cdot D_{O_2} \quad (10)$$

Tortuosity = 0.66 (fraction)

ϵ = Porosity (fraction)

S = Fraction of air filled soil pore volume at field capacity (fraction)

D_{O_2} = Oxygen diffusivity in air [m²/d]

Figure 6. Outline of oxygen balance

The adequate flux of soil oxygen is achieved by means of a balance between the amount of equivalent oxygen required by the organic matter present in the wastewater (Equation 4) and the time period needed in order to achieve the soil oxygenation by diffusive transportation, expressed in Equation 9. This balance can be observed in the framework shown in Figure 6.

3.5. Time between applications

In order to determine the time that is needed between applications of wastewater, Equation 10 is used [12]. This equation considers, in addition to the aeration time, the time that it takes to infiltrate the water in the soil (Equation 11) and the duration of irrigation.

$$t_{ap} = t_{air} + t_{in} + t_r \quad (11)$$

t_{ap} = Time between applications[d]

t_{air} = Time of aeration [d]

t_{in} = Time of infiltration [d]

t_r = Time of irrigation [d]

$$t_{in} = \frac{Ln}{k} \quad (12)$$

Ln = Hydraulic load rate (depth) [mm]

k = Infiltration or permeability in the saturated soil [mm/d]

3.6. Nitrogen balance

This balance is established through the determination of the hydraulic rate of the wastewater to be applied based on its nitrogen content; the following process differs from the design of the hydraulic load developed in Equations 1 and 2. In this case, the required hydraulic load is estimated based on the amount of nitrogen that can be removed by a crop as part of its nutritional requirements, in a determined land area and time. Equation 13 determines the nitrogen load that is to be incorporated into the soil for the crop to remove it adequately. This equation also considers the factor of nitrogen loss due to denitrification and volatilization. The result of this equation, divided by the nitrogen concentration in the wastewater, determines the hydraulic load rate as shown in Equation 14 [12].

$$L_n = \frac{U}{(1 - f)} \quad (13)$$

L_n = Nitrogen loading [kg/(ha*year)]

U = Estimated crop uptake as a function of yield [kg/(ha*year)]

f = Nitrogen loss factor (0.5–0.8) (fraction)

$$Ln_{\text{nitrogen}} = \frac{L_{\text{nitrogen}} * F}{C_{\text{nitrogen}}} \quad (14)$$

$L_{n \text{ nitrogen}}$ = Hydraulic nitrogen load based on the nitrogen load [mm/d]

C_{nitrogen} = Nitrogen concentration in the waste water [mg/l or g/m³]

F = Conversion factor

3.7. Application area

The determination of the required area for the application of wastewater in the soil is obtained from the relation between the volume of wastewater discharge and the hydraulic load rate to be applied in the soil, as shown in Equation 14 [6, 9, 12].

$$A = \frac{Q}{L_{n_d}} * F \quad (15)$$

A = Area required for the wastewater application [ha]

Q = Wastewater discharge volume [m³/d]

L_{n_d} = Design hydraulic load rate [mm/d]

F = Conversion factor

4. Case of study

In order to understand the model, a set of tests were carried out based on nine (9) potential cases, considering the following conditions:

1. The selected crop in all the cases was sugar cane.
2. For all the cases, the wastewater is used to irrigate soils with agricultural potential: Deep soils (1.5 m to 3 m), with slopes less than 15° and with a loamy texture.
3. The climate conditions are similar for all cases. The considered average precipitation is 730 mm/year.
4. The most important constituents in the wastewater to be used are: Biochemical Oxygen Demand (BOD₅), Chemical Oxygen Demand (COD), and Total Suspended Solids (TSS). For these tests, DBO₅ values of 1,000, 25,000 and 50,000 mg/l were evaluated.

The use of the model for the decision-making process begins with the input of the information related to the area selected in order to determine the site's aptitude. The aptitude is valued in a general/ global manner considering some variables such as the slope and the depth of soil and groundwater.

The software requires the input of the concentration of the constituents corresponding to the wastewater to be applied (see Table 6). Three BOD₅ concentrations (1,000, 25,000, and 50,000 mg/l) were used for the tests. Those concentrations are frequently found in the food and beverage industry effluents.

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INPUT OF WASTEWATER INFORMATION

PARAMETERS (mg / l except where noted)	Sample	PARAMETERS (mg / l except where noted)	Muestra
Temperature °C		Mercury	0.002
Fats and Oils	295.6	Nickel	0.2
Floating matter	0	Lead	0.12
Settleable Solids		Zinc	0.21
Total suspended solids		Aluminum	
Total Dissolved Solids		Beryllium	
Biochemical Oxygen Demand 5	52100	Boron	
Chemical Oxygen Demand		Cobalt	
Total Nitrogen	335.6	Fluorine	
Total Phosphorus	88.53	Iron	
Potassium	1950.72	Lithium	
Nitrates		Manganese	
Nitrites		Molybdenum	
pH	4.5	Selenium	
Fecal Coliform (MPN / 100ml)	3	Vanadium	
Helminth eggs	0	Electrical conductivity (mho / cm)	2.00
Arsenic	0.002	Sodium adsorption ratio (SAR)	2.00
Cadmium	0.05	Chlorides	2.00
Cyanides	0.03	Free residual chlorine	2.00
Copper	0.06	Water hardness	2.00
Chrome	0.13		

Discharge volume (m3 / day)

75.00

Figure 7. Input of wastewater information

Next, the software requires the input of information related to the characteristics of the soil (Figure 8). It is important to mention that the tests were performed considering loam, clay loam, and sandy loam textures for the soil. The diameter of the particles varied between 0.05 and 0.002 mm. These characteristics are related to other physical properties of the soil such as porosity and infiltration.

Additionally, the model requires information related to the type of crop present and the climatic conditions of the environment. For the performance tests, sugar cane crops with average precipitation conditions (730mm/year) were considered.

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Input of Soil Characteristics

PARAMETERS	Sample
Moisture Retention	
Texture	Franco Arenoso
Porosity (%)	42.00
Field capacity (%)	25.21
Permeabilidad (mm/d)	276.48
Soil fertility	
Organic Matter (%)	1.91
Electrical conductivity (mmhos / cm)	0.27
pH	7.20
Total Nitrogen (ppm or mg / l)	850.00
Available phosphorus (ppm or mg / l)	23.10
Available potassium (ppm or mg / l)	583.21
Salinity and sodium (saturation extract)	
Electrical conductivity (mS / cm)	0.83
pH	7.30
Sodium adsorption ratio	0.96
Exchangeable Sodium (%)	10.32
Cation exchange capacity (meq / 100g of :)	25.30

Figure 8. Input of soil characteristics

Once the information input is completed, the model calculates the optimum parameters for the wastewater application based on the available information. Figure 9 shows an example of the obtained results.

Figure 9. Advanced results

The results obtained from all performed tests in the hypothetical cases are detailed in Table 6. Those results show the model estimates of the required surface for the application and the estimated time lap between applications in order to achieve an adequate use of the nutrients provided by the wastewater, which will be required for the crop development.

TEST	BOD [mg/l]	Texture	Surface (Ha)	Time (h)
1	1000	Loam	0.11	6.48
2	1000	Sandy Loam	0.14	5.76
3	1000	Sandy Loam	0.10	11.28
4	25000	Loam	4.03	22.32
5	25000	Clay Loam	4.63	16.8
6	25000	Clay Loam	4.66	46.56
7	50000	Loam	9.18	50.64
8	50000	Clay Loam	7.91	28.8
9	50000	Clay Loam	14.89	149.04

Table 6. Model tests results

The analysis of the results of the tests from the STAR ASA model could determine that the higher the concentration of organic matter in the wastewater, the larger the requirement of agricultural area. However, this quantity depends strongly on the characteristics of the soil. The smaller the soil particle size, the smaller the required area (Figure 10).

Figure 10. Results — application surface

The time required between wastewater applications depends mostly on the soil's characteristics. The smaller the particle size, the shorter the required time lap (Figure 11). This result is related to the infiltration capacity of the soils. The larger the particle size, the smaller the water retention period in the agricultural areas. Therefore, frequent application on sandy soils can cause the lixiviation of the nutrients and chemicals into the groundwater.

Figure 11. Results — time period between applications

5. Conclusions

The STAR ASA model was able to integrate the characteristics of the wastewater and the soil, as well as the nutritional requirements of the crops and the environmental regulations, by means of mathematical models selected to evaluate the feasibility of the application of wastewaters with a high content of organic matter with agricultural soil irrigation. The model allowed the estimation of the hydraulic load rate, the time lap between applications, and the amount of nutrients provided to the soil.

Based on the theoretical analysis of the used models, it was determined that the controlled application of wastewater allows the filtration and degradation of the constituents with a high content of organic matter that were applied to the soil, as long as the parameters recommended by the STAR ASA model are fulfilled.

Finally, considering the characteristics of the analysed wastewaters, the characteristics of the selected soils, and the nutritional requirements of the sugar cane, it was determined that for

the test cases, the application of the effluents in the soil will contribute to fertilization, specifically nitrogen-related fertilization. However, it needs to be clarified that the results obtained in this study cannot be generalized to other type of effluent without previous analysis. The wastewaters, the agricultural soils, the climatic conditions, and the crops requirements may be different.

6. Recommendations

Considering this research as starting point, it is recommended to apply the model in additional case studies, for industries with wastewaters with different concentrations and constituents, in order to determine the behaviour of the application on those conditions to carry out the necessary modifications.

It is recommended to perform a study to determine the effect of the long-term application of organic matter versus the microbial respiration, as a complement for this research.

Monitoring is of vital importance for the correct application of effluents; consequently, it is recommended to perform control measurements at least every six months.

It is recommended to carry out an adequate dimensioning of the storage system of wastewater in containers considering the climatic conditions and the crop type, in order to avoid ponding, runoffs, leaching, and erosion in high precipitation and harvesting seasons.

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