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Comparative study between biological treatment and a physicochemical treatment for the removal of Butyl Acetate in industrial residual effluents

Estudio comparativo entre un tratamiento biológico y un tratamiento fisicoquímico para la remoción de Butil Acetato en efluentes residuales industriales

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Abstract

A comparison was made between a fixed aerobic biological process and a physicochemical treatment for waste effluents with butyl acetate. An acrylic tank with 100 L capacity and a support medium for PET bottles was implemented for the formation of the biofilm and thus develop the biological reactor. In the experimental phase, concentrations of 10, 20 and 30% of butyl acetate containing sample, using hydraulic retention times of: (16, 8, 5.33 and 4 days) for each concentration. After the experimentation, a removal of 99% of COD and 97% of BOD was obtained. For the physicochemical treatment, coagulant, flocculant, and adjuvants were used, by a jar test. A decrease in 74%, 53.8%, 55%, 97% and 37%, for electrical conductivity, total suspended solids, color, turbidity, COD and BOD respectively, were obtained compared to the initial sample. Both treatments were filtered through a bed packed with activated carbon, sand, and silica gravel. The aim of this work was to evaluate / quantify butyl acetate removal efficiency in each treatment for its subsequent comparison, with prospect to the reduction of similar pollutants in residual effluents is intended.

Biological treatment, Physicochemical treatment, Butyl acetate

Resumen

Se realizó una comparación entre un proceso biológico aerobio fijo y un tratamiento fisicoquímico para efluentes residuales con butil acetato. Para el desarrollo del reactor biológico se implementó un tanque de acrílico con capacidad de 100 L y un medio de soporte de botellas PET para la formación del biofilm, en la parte experimental se manejaron concentraciones de 10, 20 y 30 % de la muestra con butil acetato, empleando tiempos de retención hidráulica de: (16, 8, 5.33 y 4 días) para cada concentración. Finalizada la experimentación se obtuvo una remoción del 99% de DQO y 97 % de DBO. Para el tratamiento fisicoquímico se empleó coagulante, floculante y coadyuvantes, mediante una prueba de jarras. Obteniendo como resultados la disminución en un 74 %, 53.8 %, 55 %, 97 % y 37%, para conductividad eléctrica, solidos suspendidos totales, color, turbidez, DQO y DBO respectivamente, en comparación a la muestra inicial. Ambos tratamientos se filtraron mediante un lecho empacado con carbón activado, arena y grava sílica. El objetivo del presente trabajo fue evaluar/cuantificar la eficiencia de remoción del butil acetato en cada tratamiento para su posterior comparación, por lo cual se pretende la reducción de contaminantes similares en efluentes residuales.

Tratamiento biológico, Tratamiento fisicoquímico, Butil acetato

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Introducción

Surface water and groundwater pollution is reported at 24% and 4% respectively, which has been generated by high concentrations of various chemical species. These come from diffuse sources of pollution (use of pesticides, manure production in agriculture) and specific sources (industrial landfills, as well as in industrial mining practices).

Effluents from industrial processes contain toxic products, harmful organic compounds, and metals, of varying composition, type and concentration, depending on the processes that generate them. Natural organic compounds in the environment tend to naturally degrade slowly into less harmful components, however, volatile organic compounds (VOCs) found in effluents from industrial processes are not considered biodegradable.

VOCs are used in the manufacture of paints, varnishes, waxes and are chemical industry's main organic pollutants used as solvents, being butyl acetate (C6H12O2), most widely used, as a solvent in polyurethane resins and paints (stripping) for special applications. It is a colorless liquid with a fruity odor, soluble in organic solvents, highly flammable, and dangerous to health, affecting the central nervous system.

It has been reported in various studies that water contaminated with compounds like butyl acetate, such as ethyl tert-butyl ether ($C_6H_{14}O$), methyl tert-butyl ether ($C_5H_{12}O$), tert-amyl methyl ether (C6H14O) and diisopropyl ether (C6H14O), have been treated by using microorganisms in a biodegradation process. Because it is a slow process, the addition of specific bacteria selected for their efficiency in removing contaminants has been implemented.

Residual water

Wastewater can be classified according to its origin: industrial, commercial, and domestic sector, in some cases adequate treatments are not implemented for its reuse, which, depending on current regulations and the economic interest of each company, is the importance given to the treatment process.

The pollutants concentration present in wastewater varied according to the origin of the sample and industrial use, suspended solids, organic matter, oils, fats, nitrogen, and phosphorus can be found. Membrane activated carbon filtration and chemical precipitation techniques are the most used for its recovery.

Types of wastewater treatment

The treatments most used in wastewater purification processes are primary, secondary, and tertiary, the conditions, on which, the choice of a treatment is based are the flow rate to treat, the concentration of pollutants, the type of pollutants, the place weather and the continuity in the raw water supply, the treatments are described below:

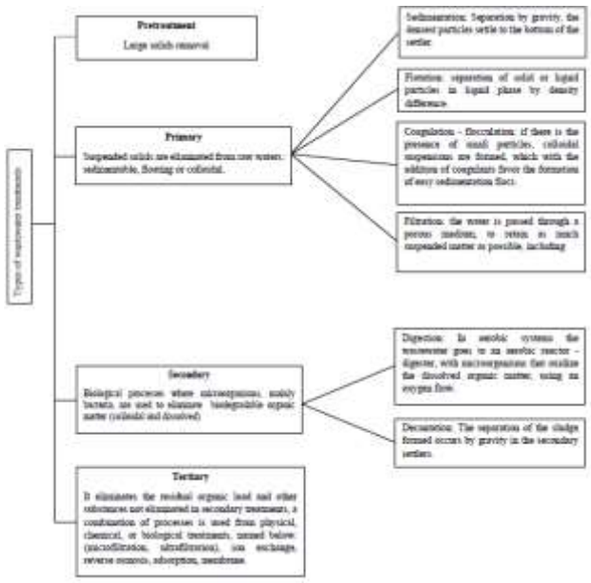

Figure 1 General water treatment diagram
Own Elaboration

Another treatment is disinfection, which consists of eliminating or inactivating pathogenic microorganisms or any other living microorganism to ensure the reuse of treated water. The main disinfection processes are chlorination, ozonation, electro-disinfection.

Methodology
Reactor development

A 100 L capacity acrylic tank was used, with the following dimensions (60 cm x 56 cm x 30 cm), which was adapted as a reactor. Two valves were placed after the feed inlet, a sphere type with a diameter of 1.5 inches, flow 3.95 L sec^{-1}, to regulate the feed flow of the affluent through the upper and lower part of the reactor.

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To regulate the effluent outflow and the biomass purge, two ball valves were used as previously described. The sludge was recirculated with a MAXIMA® aeration pump for 113.6 L, which were connected to three 45 cm long porous rubber diffuser hoses, fish tank type to maintain a dissolved oxygen concentration of 3-4 mg L^{-1} arranged at the bottom of the tank.

Support medium

108 polyethylene terephthalate (PET) bottles of different capacities (2, 1 and 0.5 L) with holes were used to facilitate air flow. They were placed concentrically (they were assembled from smaller to larger capacity) and were distributed in an organized way in the bioreactor to allow the flow of the water, thus avoiding the obstruction of this, to increase the contact surface and the development of the biofilm, such as can be seen in Figure 2.

Figure 2 Fixed aerobic biological reactor prototype

Biological process development

For the formation of the biofilm in the reactor, 3 L of activated sludge inoculum from the treatment plant of the Autonomous University of Querétaro, Airport campus, were used. The sludge was fed with residual water from the same plant of the institution collected from laboratories and bathrooms, for a period of 1 to 6 months for maintenance, adaptation, and formation of biofilm in the PET support, as observed in Figure 3.

Figure 3 Biofilm formation

After establishing the biofilm and being able to guarantee the efficiency of the system in reducing nutrients, BOD / COD degradation and pH stabilization, the effluent quality analysis was carried out to verify compliance with NOM-003-ECOL-1997 and NOM-001-SEMARNAT-96.

Biokinetic coefficients

To evaluate the efficiency of the reactor and the stabilization of the biomass, the biokinetic coefficients were determined (Equation 1), which indicate the growth of the biomass, the use rate of the substrate, the food-microorganism relationship, and the mean time of cell retention. Equation to calculate the mean speed constant (Ks).

$$\frac{\theta X}{S_0 - S} = \frac{K_S}{(k)(S)} + \frac{1}{k} \quad (1)$$

Where:
θ = hydraulic retention time (h)
X = concentration of volatile suspended solids in the mixed liquor, L / h, mg VSS ML / L / h
S_0 = concentration of soluble COD in influent (mg L^{-1})
S = concentration of soluble COD in effluent (mg L^{-1})
k = maximum substrate utilization rate (h)
Ks = mean speed constant (mg L^{-1})

Equation 2 to calculate maximum cell yield (Y) and endogenous decay coefficient (kd)

$$\frac{1}{\theta_C} = Y \frac{S_0 - S}{X\theta} - k_d \quad (2)$$

Where:
Y = maximum cell yield
kd = endogenous decay coefficient, h^{-1}

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Subsequently, contaminant elimination from the test sample was sought using microorganisms adapted to the residual water in the reactor in a period of 1 to 6 months.

Calculation of the contact area of the biofilm

To calculate the contact area of the microorganisms to the PET support, the following equations were used for the truncated cone (3) and cylinder (4):

$$A = \pi\left(R_1^2 + R_2^2 + a(R_1 + R_2)\right) \quad (3)$$

$$A_c = b\ x\ h = (2\pi\ \mathrm{r})\ (\mathrm{h}) \quad (4)$$

Adaptation of the effluent aerobic biological process (ABP) with butyl acetate

For the beginning of this adaptation stage, it was carried out by adding the effluent with butyl acetate to the biological reactor. Three concentrations were used (10, 20 and 30%) diluted in residual water, the process was carried out for four months, as shown in Figure 4 and 5.

Figure 4 Biological reactor feeding with domestic wastewater and effluent with butyl acetate mixture

Figure 5 Biological reactor adaptation to the effluent with butyl acetate

Hydraulic retention times

The different hydraulic retention times applied were 16, 8, 5.33 and 4 days for each of the concentrations used (10, 20 and 30%) of wastewater and effluent with butyl acetate.

Deveopment of the physicochemical process

For the physicochemical process, 10 experiments were carried out using the jar test for the coagulant, flocculant, and adjuvants, which were carried out on a shaker (PHIPPS & BIRD, USA), for testing 6-place jars with six 1 L beakers, the stirring time was 5 min at 150 rpm. The initial pH of the samples was 3.6.

Table 1 summarizes the methodology applied, as well as the concentrations used in the reagents to perform the jar tests.

Test	Conditions
1	pH 3.6-9, 45 ml chemical lime (20%), 5 ml metal precipitator (1%), 2 ml coagulant 90/10 (10%), 5 ml flocculant 70/24 (1%)
2	pH 3.6-2, 1.8 ml of H2SO4 (98%), 2 ml metal precipitator (1%), pH 7, 45 ml chemical lime (20%), 2.5 ml coagulant 90/10 (10%), 1.3 ml flocculant 70/24 (1%)
3	pH 3.6- 6, 30 ml chemical lime (20%), 3 ml metal precipitator (1%), 1.5 ml coagulant 90/10 (10%), 2 ml flocculant 70/24 (1%)
4	pH 3.6- 8, 40 ml chemical lime (20%), 7 ml metal precipitator (1%), 4 ml coagulant 90/10 (10%), 7 ml flocculant 70/24 (1%)
5	pH 3.6-1, 2.8 ml H2SO4 (98%), 3 ml metal precipitator (1%), pH 7, 60 ml chemical lime (20%), 2 ml coagulant 90/10 (10%), 8 ml of flocculant 70/24 (1%)

Table 1 Conditions applied at jar tests

Filtration system

A 60 cm acrylic column and a diameter of 10 cm was run. It was packed with activated carbon, sand, and silica gravel 1-1 ½ cm, using layers of 15 cm of each, the result obtained is shown in Figure 6.

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Figure 6 Physicochemically treated sample before and after filtration

The samples after the biological and physicochemical treatment were subjected to a filtration process and the result is shown in Figure 7.

Figure 7 Filtered samples after biological treatment (1, 2 and 3) and physicochemical treatment (4)

Analytical techniques

The analyzes of pH, conductivity, chemical oxygen demand (COD), total dissolved solids (TDS), total solids (ST) and color (Pt-Co), were applied for both treatments.

Results

Biological treatment: Domestic wastewater characterization

Parameter	Value obtained	Maximum allowable limit
Temperature °C	25.5	40 °C
Fats and Oils	25	25 mg/L
Floating Matter	Ausente	Ausente
Settling Solids	3	2 mg/L
Total Suspended Solids	500	60 mg/L
Biochemical Oxygen Demand	600	60 mg/L
Total Nitrogen	50	25 mg/L
Total Phosphorous	20	10 mg/L
Arsenic	N.D.	0.2 mg/L
Cadmium	N.D.	0.2 mg/L
Cianide	N.D.	2.0 mg/L
Copper	N.D.	6.0 mg/L
Chromium	N.D.	1.00 mg/L
Mercury	N.D.	0.01 mg/L
Níckel	N.D.	4.0 mg/L
Lead	N.D.	0.4 mg/L
Zinc	N.D.	20 mg/L

Table 2 Characterization of NOM-001 SEMARNAT 1996

Parameter	Value obtained	Maximum allowable limit
Fecal coliforms	≥2400000 NMP	240 NMP/100 ml
Helmith eggs	< 1	< 1 (h/1)
Fats and oils	25	15 m/l
BOD_5	594	20 mg/l
TSS	500	20 mg/l

Table 3 Characterization of NOM-003 SEMARNAT 1997

Biokinetic constant

Obtaining the Chemical Oxygen Demand (S) and Volatile Suspended Solids (X), associated with the calculation of the biokinetic coefficients, shown in Table 4.

Cycle	S_0	S	$\theta = \theta_c$	X
	g/L COD	g/L COD	h	g VSS/L
1	0.795	--	0	5.00
2	--	0.284	1	4.86
3	--	0.176	2	4.53
4	--	0.154	4	3.5
5	--	0.138	8	2.30

Table 4 Chemical Oxygen Demand (S) and Volatile Suspended Solids (X)

To obtain the maximum substrate utilization rate (k) and the average speed constant (Ks), the data obtained from Table 5 was first plotted with calculations of the equation Y.

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Xθ g VSS/h*L	1 /S $(h)^{-1}$	Xθ/(S₀ – S) h^{-1}
4.86	3.533	9.0005
9.06	5.6818	14.3711
14	6.4935	16.4003
18.4	7.2463	18.2825

Table 5 Variables associated with the calculation of k and Ks

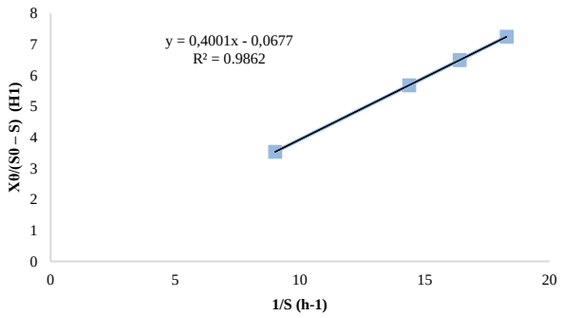

Figure 8 Maximum growth rate (k) and Average growth rate (Ks)

Figure 8 is the graph of Xθ / (S0 - S) according to 1 / S. In this graph the ordinate to the origin is 1 / k, and the slope is equal to Ks / k. Thus, obtaining k and Ks were 5.91 h^{-1} and 14.78 g / L respectively.

Maximum cell yield (Y) and endogenous decay coefficient (kd)

The variables 1 / θc and (S_0 - S) / Xθ were obtained based on the data shown in table 6. The graph of these results to obtain the biokinetic coefficients: Maximum cell yield (Y) and the endogenous decay coefficient (kd) is shown in Figure 9.

$1/\theta_c$ h^{-1}	$(S_0 – S)/ X\theta$ h^{-1}
1	0.112
0.5	0.067
0.25	0.048
0.125	0.037

Table 6 Variables associated with the calculation of Y and Kd

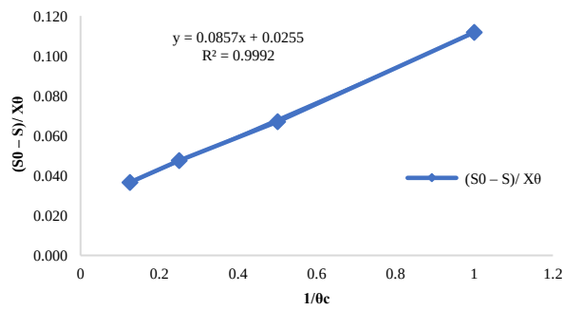

Figure 9 Maximum cell yield (Y) and endogenous decay coefficient (kd)

Coefficients	Result obtained
Substrate utilization rate (k) g CODs / gVSS	5.91
Average rate constant (Ks) mg / l CODs	14.78
Maximum cell yield (Y) mg VSS / mg CODs	0.085
Endogenous decay coefficient (kd) g SSV / g VSS	0.025

Table 7 Results obtained from the biokinetic coefficients of the biological reactor

Once 1 / θc was graphed with respect to (S0 - S) / Xθ, the ordinate to the origin kd was obtained and the slope is Y. Consequently, the values of Y and kd that were obtained were 0.085 and 0.025 h-1 respectively.

Biofilm formation

The sum of the area of the truncated cone and the cylinder resulted in 0.604262 m^2 and the total contact area of the system for the reactor was 10.272454 m^2.

Hydraulic retention

The parameters established in NOM 003 SEMARNAT 1997 were analyzed for the different hydraulic retention times in each concentration, as shown in Table 8 (a, b and c).

Holding time (days)	COD (mg/L)	BOD (mg/L)	TSS (mg/L)	Fats and oils (mg/L)	Fecal coliforms (NMP/100 ml)	Helminth Eggs (Organismos/L)
16	16	12.90	9	<1.0	<3.0	Absent
8	14	14.32	12	<1.0	<3.0	Absent
5.33	18	17.56	15	<1.0	<3.0	Absent
4	19	18.7	14	<1.0	<3.0	Absent
Maximum allowable	N.E.	20	20	15	240	<1.0

Table 8 a 10 % concentration

Holding time (days)	COD (mg/L)	BOD (mg/L)	TSS (mg/L)	Fats and oils (mg/L)	Fecal coliforms (NMP/100 ml)	Helminth Eggs (Organismos/L)
16	16	18.49	13	<1.0	<3.0	Absent
8	19	19.16	12	<1.0	<3.0	Absent
5.33	15.51	19.38	13	<1.0	<3.0	Absent
4	18.51	21.45	12	<1.0	<3.0	Absent
Maximum allowable	N.E.	20	20	15	240	<1.0

Table 8 b 20 % concentration

Holding time (days)	COD (mg/L)	BOD (mg/L)	TSS (mg/L)	Fats and oils (mg/L)	Fecal coliforms (NMP/100 ml)	Helminth Eggs (Organismos/L)
16	19	14.4	12	<1.0	<3.0	Absent
8	10	12.75	10	<1.0	<3.0	Absent
5.33	15	16.23	11	<1.0	<3.0	Absent
4	19	19.62	14	<1.0	<3.0	Absent
Maximum allowable	N.E.	20	20	15	240	<1.0

Tabla 8 c 30 % concentration

Physicochemical treatment

The results are shown in Table 9, of the parameters characterized before and after the physicochemical treatment.

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Parameter	Unit	Initial result	Final result
Electric conductivity	µS	13925	7298
Total suspended solids	mg/L	1390	360
Color	Pt-Co	934	432
Turbidity	NTU	756	340
COD	mg/L	35720	959
BOD	mg/L	900	300
pH	N/A	3.2	7

Table 9 Industrial wastewater characterization

Conclusions

Physicochemical treatment

The parameters analyzed after treatment were decreased by 74%, 53.8%, 55%, 97% and 67%, for electrical conductivity, total suspended solids, color, turbidity, COD and BOD respectively, compared to the initial sample.

Biological treatment

The parameters analyzed in the different hydraulic retention times in the experimental part for COD was 99%. As well as they also present the values of BOD 97%, for all the values. Regarding compliance with NOM 003 SEMARNAT 1997, all retention times comply except for the retention time of 3.2 days for the 30% concentration with wastewater and effluent with butyl acetate

In both treatments there was COD reduction, which indicates that there is a significant removal percentage for butyl acetate. The comparison of the treatments applied to the effluent showed that the biological treatment presented greater removal of the pollutant before the physicochemical treatment in 2% of COD and 30% of BOD.

Discussion

A mass coupled gas spectroscopy analysis is recommended to confirm the removal of butyl acetate in the effluent or the transformation into other chemical species.

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