Chapter 1

Biodegradability of Water from Crude Oil Production

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1. Introduction

According to Gutiérrez *et al.* (2007) the waters of formation (WOF), are those that are naturally in the rocks and are present before the perforation of the well. Their composition depends on the origin of the water and the modification that could happen as soon as they enter in contact with the environment of the subsoil. WOF must be obtained from the bottom of the well; nevertheless, for costs reason the samples are taken at the surface level, in the head of the well. As they rise in the column from the well up to the surface, their characteristics change due to the changes of pressure, temperature and composition of the gases. For this reason the name adapted for these samples of waters is water associated with crude oil production. Other researchers name these waters as water from petroleum, water from oil field production, oily waters, effluent from the extraction of oil, water from petroleum. In this work they are named waters associated with crude oil production (WCP).

Among the characteristics of WCP are their high content of free and emulsified crude oil and hydrocarbons, suspended solid, H_2S and mercaptans (Gutiérrez *et al.*, 2002), aromatic, poliaromatic and phenols compounds (Rincón *et al.*, 2008), high temperature and high salinity (Guerrero *et al.*, 2005; Li *et al.*, 2005), saturated, aromatics, resins and asphaltenes compounds (SARA) (Díaz *et al.*, 2007), and metal traces Na, Ca, Mg, Fe, Sr, Cr, As and Hg (Gutiérrez *et al.*, 2009). According to García *et al.* (2004) among the pollutants with a major potential impact related to the petroleum industry are polycyclic aromatic hydrocarbons (PAH), voltaic organic compounds (VOC) and total hydrocarbons of the oil (THO). The first ones have high carcinogenic, mutagenic and teratogenic potential in aquatic organisms; the second ones contribute to the greenhouse effect and are involved in the direct ozone formation on the soil level and indirectly on the acid rain, besides some individual compounds are toxic, carcinogenic, mutagenic or bioaccumulative, and the last ones present diverse effects on the flora an fauna.

Gives that the WCP volumes generated in the Ulé tank farm, on the east cost of Maracaibo Lake, Venezuela, belonging to the petroleum industry in Venezuela, would exceed the needs for secondary recovery and the systems of reinjection would be rapidly saturated, different research works were realized to present alternatives to the petroleum industry, to diminish the potential pollutant of WCP.

In this aspect, some proposals for the treatment of WCP are aerobic and anaerobic biological processes, physicochemical treatment and some new technologies as constructed wetlands. Among the anaerobic processes are the batch reactors (BR) and the upflow anaerobic sludge blanket reactors (UASB).

The biological mesophilical and thermophilical anaerobic systems have been successful in the treatment of complex waters, with low, moderate and high organic load (Lettinga, 2001). In the case of UASB, these reactors are outlined by their capacity to retain biomass, to form granular sludge with high properties of sedimentation, to handle high organic load to short hydraulic retention time (HRT), produce biogas and remove high concentration of biodegradable organic matter (Lepisto and Rintala, 1990; Lettinga, 2005).

On the other hand, the aerobic systems have been efficient for the treatment of wastewater containing chemical compounds resistant to be biodegraded. Among these systems are the sequential biological reactors (SBR), which have showed excellent results in the degradation of toxic compounds present in industry effluents (Díaz *et al.*, 2005a; González *et al.*, 2007). As well as, the rotating biological contactor reactors (RBC), which produce good quality effluents including total nitrification, low costs and ease of operation and maintenance (Behling *et al.*, 2003).

Among the physicochemical treatment applied to reduce the pollutants in wastewater are the dissolve air flotation (DAF) and the coagulation. The most applied products to treat natural water and wastewater by coagulation and flocculation are iron and aluminium salts. However, the cationic polymers have demonstrated their efficiency in the removal of oils and phenols from industrial wastewater (Renault *et al.*, 2009; Ahmad *et al.*, 2006).

In this investigation was reviewed a several papers from studies conducted at the Universidad del Zulia during 2002 to 2012, to analyze the efficiency of biological and physicochemical systems BR, UASB, SBR and RBC, and the physicochemical treatment as coagulation and flotation (DAF), which have been evaluated to remove COD, hydrocarbons, SARA and phenols, present in the WCP.

The instrument used was a matrix register of the treatment, considering criteria like WCP type, system of treatments, operation conditions, organic load, retention times, temperature, pollutant contents and dose of coagulant. The efficiency of the treatments was compared considering the parameters COD, phenols, hydrocarbons and SARA.

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2. Results

2.1. Origin and composition of the waters associated with the crude oil production

The WCP samples were obtained from the Ulé tank farm, located on the east coast of Maracaibo Lake, Tía Juana, Zulia state, Venezuela (Figure 1). The water samples come from the segregations: Tía Juana light (TJL), Urdaneta heavy (UH), Tía Juana medium (TJM), and the dehydrations of the Punta Gorda tank farm (Rosa medium-RM), Shell Ulé (F-6/h-7) and lacustrine terminal of La Salina (LTLS). These waters were obtained from the separation of the water associated with the extraction of light crude oil (>31.8ºAPI) WCPL, from the water associated with the extraction of medium crude oil (22ºAPI-29.9ºAPI) WCPM, from the water associated with the extraction of heavy crude oil (10ºAPI-21.9ºAPI) WCPH, classified according to the American Petroleum Institute. Also, water samples were taken from the converged point of the three cuts (WCPC).

The Tables 1, 2, 3 and 4 present the principal characteristics of WCPL, WCPM, WCPH and WCPC, respectively. In general, it is observed that the physicochemical characteristics of the WCP are different depending on the contact of these waters with the crude oil associated. They are waters with high pollutant contents and they do not comply with the Venezuelan environmental regulations to be discharged into water bodies (Gaceta Oficial, 1995). On the other hand, the differences in the characteristics reported by the researchers, might be related to the changes that have been given in the productive processes of the petroleum industry in the last years.

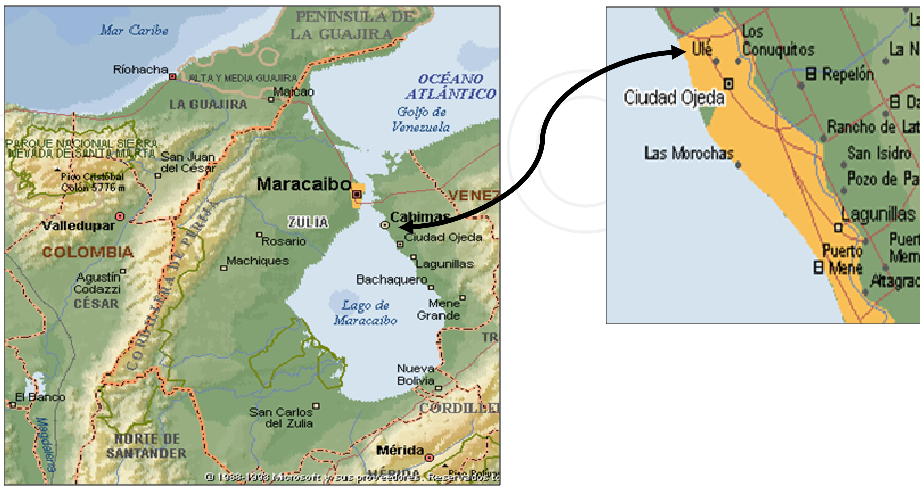

Figure 1. Geographical location of the Ulé tank farm, Tía Juana Zulia state, Venezuela.

Parameters	Díaz *et al.* (2005a)	Díaz *et al.* (2005b)	Gutiérrez et al. (2012)	González et al. (2007)	Rincón et al. (2008)
pH	7.9	8.0	8.3	7.99	NR
Alkalinity (mg $CaCO_3$/L)	2933	2215	2670	2412	NR
COD soluble (mg/L)	1065.2	799	1400	1105	106.2
Phenols (mg/L)	19.36	1.73	NR	16.8	NR
Nitrogen NTK (mg/L)	23.82	28.8	20	21.2	23.82
Phosphorous (mg/L)	1.07	1.0	2.2	1.57	1.07
Hydrocarbons (mg/L)	NR	91	224.2	78.0	NR
Chlorines (mg/L)	NR	NR	NR	NR	NR
TSS (mg/L)	NR	NR	104	NR	NR
VSS (mg/L)	NR	NR	54	NR	NR
O&G (mg/L)	NR	NR	66	100.7	NR
Saturated (mg/L)	NR	NR	76.6*	NR	1.24
Aromatics (mg/L)	NR	NR	7.04*	NR	17.64
Resins (mg/L)	NR	NR	6.34*	NR	8.51
Asphaltenes (mg/L)	NR	NR	7.73*	NR	7.49

*Values in (%), NR: No register

Table 1. Physicochemical parameters of WCPL from tank farm of Ulé

Parameters	Díaz *et al.* (2005a)	Gutiérrez et al. (2012)	Rincón et al. (2008)	Castro et al. (2008)
pH	8.0	8.5	NR	8.04
Alkalinity (mg $CaCO_3$/L)	3440	2800	NR	2906
COD soluble (mg/L)	782.6	933	782.6	880
Phenols (mg/L)	1.40	NR	NR	NR
Nitrogen NTK (mg/L)	39.20	15.1	39.20	NR
Phosphorous (mg/L)	1.05	3.5	1.05	NR
Hydrocarbons (mg/L)	NR	148.7	NR	NR
Chlorines (mg/L)	NR	NR	NR	NR
TSS (mg/L)	NR	NR	NR	82.57
VSS (mg/L)	NR	NR	NR	69.71
Saturated (mg/L)	NR	25.32*	5.73	0.24

Parameters	Díaz *et al.* (2005a)	Gutiérrez et al. (2012)	Rincón et al. (2008)	Castro et al. (2008)
Aromatics (mg/L)	NR	5.86*	9.77	50.34
Resins (mg/L)	NR	6.49*	5.30	33.22
Asphaltenes (mg/L)	NR	5.99*	5.30	16.10

*Values in (%), NR: No register

Table 2. Physicochemical parameters of WCPM from tank farm of Ulé

Parameters	Díaz *et al.* (2005a)	Gutiérrez et al. (2012)	González et al. (2007)	Gutiérrez et al. (2009)	Caldera et al. (2011)
pH	8.0	8.2	8.3	7.08	8.41
Alkalinity (mg $CaCO_3$/L)	885	1000	885	NR	803.33
COD soluble (mg/L)	307	864	320	1029	259.6
Phenols (mg/L)	2.70	NR	2.5	NR	0.83
Nitrogen NTK (mg/L)	10.61	15.7	9.2	8.26	5.60
Phosphorous (mg/L)	2.68	2.0	9.8	0.013	3.01
Hydrocarbons (mg/L)	NR	52.7	78	35.0	123.21
Chlorines (mg/L)	NR	NR	NR	NR	1101.21
TSS (mg/L)	NR	NR	NR	NR	573.33
VSS (mg/L)	NR	NR	NR	NR	220.00
Color (CU)	NR	NR	NR	NR	718.80
Turbidity (NTU)	NR	NR	NR	NR	140.00
Chrome (mg/L)	NR	NR	NR	4.75	NR
Lead (mg/L)	NR	NR	NR	4.35	0.0
Sodium (mg/L)	NR	NR	NR	89.94	NR
Zinc (mg/L)	NR	NR	NR	2.50	0.30
O&G (mg/L)	NR	NR	113.3	NR	NR
Saturated (mg/L)	NR	23.97*	NR	NR	NR
Aromatic (mg/L)	NR	6.15*	NR	NR	NR
Resins (mg/L)	NR	64.7*	NR	NR	NR
Asphaltenes (mg/L)	NR	5.14*	NR	NR	NR

*Values in (%). NR: No register

Table 3. Physicochemical parameters of WCPH from tank farm of Ulé

Parameters	Behling et al. (2003)[a]	Rincón *et al.* (2004)[a]	Rojas *et al.* (2008)[b]	Blanco *et al.* (2008)[c]
pH	7.72	8	7.74	8.03
Alkalinity (mg $CaCO_3$/L)	2460	2238	2477	2635
COD soluble (mg/L)	823	NR	NR	1391.85
COD total (mg/L)	NR	700	NR	NR
Phenols (mg/L)	NR	5	NR	2.14
Nitrogen NTK (mg/L)	12.92	NR	NR	17.55
Phosphorous (mg/L)	1.40	NR	NR	3.67
Hydrocarbons (mg/L)	NR	100	NR	276.68
Chlorine (mg/L)	NR	NR	1802	1404.87
TSS (mg/L)	170	NR	122	550
VSS (mg/L)	50	NR	NR	82.35
Sulfides (mg/L)	NR	NR	NR	7.32
Turbidity (NTU)	NR	NR	480	NR
Chrome (mg/L)	NR	NR	NR	0.31
Lead (mg/L)	NR	NR	NR	0.17
Sodium (mg/L)	NR	NR	NR	8880.32
Nickel (mg/L)	NR	NR	NR	0.20
Zinc (mg/L)	NR	NR	NR	0.32
Copper (mg/L)	NR	NR	NR	0.19
O&G (mg/L)	NR	181	737	NR

[a] Combination of light, medium and heavy crude oil, and exit of the clarifier

[b] Combination of medium and heavy crude oil, API 5.

[c] Combination of light, medium and heavy crude oil, and in of the clarifier

NR: No register

Table 4. Physicochemical parameters of WCPC from tank farm of Ulé

2.2. Treatment of the waters associated with crude oil production

The Tables 5, 6, 7 and 8 show a summary of the methodology used by each researcher, showing the operational conditions for each system. On the other hand, Table 9 and Table 10 compare the different treatments: physicochemical treatments, aerobic and anaerobic biological treatment, and combined treatments.

2.3. Biological treatment applied to the waters associated with crude oil production

The Tables 5 and 6 show a resume of the aerobic and anaerobic biological treatments applied to WCP, and Table 8 shows the operation conditions of the combined system aerobic-anaerobic applied to WCP. Among the aerobic biological systems are the rotating biological contactor reactors (RBC), the sequential biological reactors (SBR) and the continuous flow reactors (CR); and among the anaerobic biological treatments are the batch reactors (BR) and the upflow anaerobic sludge blanket reactors (UASB), working under mesophilic and thermophilic conditions. Likewise, Table 9and Table 10 present a summary of the results of applying these treatments to WCP.

Researcher, year	Kind of WCP	Treatment systems	Characteristics of the experimental equipment	Operation conditions	Parameters evaluated
Behling *et al.* (2003)	WCPC (WCPL, WCPM and WCPH)	RBC	RBC of 9.5 L, with 50 circular disc of PVC, 0.8 cm separation, supported in an axis of carbon steel 3/8 ” diameter, rotation speed of 2.5 rpm. The discs were immersed 40 % in the effluent. The area of contact was 2.44 m^2. The water volume was 7.5 L	The RBC worked under mesophilic condition. The organic load average applied was 2.04 ± 0.7 g COD/m^2d and 5.2 mL/min, TRH of 24 h, temperature 27-32ºC.	pH COD TSS VSS Total alkalinity
Díaz *et al.* (2005a)	WCPL, WCPM and WCPH	SBR	The SBR of 4 L were constructed in material of plastic and cylindrical form, with a volume of operation of 2 L, in which 600 mL sludge and 1.4 L of WCP. At the bottom of the reactors were located air diffusers connected to a compressor.	After acclimated and stabilized, they worked with HRT of 16 hours with sequence of 15 hours of ventilation, 30 minutes of sedimentation and 30 minutes for capture of sample and recharges of the reactor. The temperature was mesophilic (37 ºC). The SBR-1, SBR-2, SBR-3 operated with organic charges of 1.6; 1.17 and 0.46 kg/m^3d for the WCPL, WCPM and WCPH, respectively.	pH Alkalinity COD Phenols
Díaz *et al.* (2005b)	WCPM	SBR	The SBR of 2 L was constructed in material of plastic, with 600 mL of sludge and 1.4 L of WCPM. They gave oxygen to the reactor by means of a compressor.	After acclimated and stabilized, they were operated at the first stage of 15 hours the HRT and time of cellular retention of 15-20 days with sequence of 14 hours for mixed, ½ hour of rest and ½ hour for discharge and load. Whereas in the second stage the HRT was 24 hours with sequence of 23 hours for mixed and ventilation and one hour of discharge and load. The temperature was 37 ºC. The	COD Hydrocarbons Phenols

Researcher, year	Kind of WCP	Treatment systems	Characteristics of the experimental equipment	Operation conditions	Parameters evaluated
				organic load applied was between 0.89 and 0.51 kg/m^{3}d	
González *et al.* (2007)	WCPL and WCPH	SBR	The SBR of 2 L was constructed in material of plastic, in cylindrical form, in which they added 600 mL of sludge and 1.4 L of WCP. They gave oxygen to the reactor by a compressor.	HRT of 8 hours and time of cellular retention of 20 days. Nutrients were added. The COD in the inflow was 1105 and 320 mg/L for WCPL and WCPH, respectively.	COD Hydrocarbons Phenols
Castro *et al.* (2008)	WCPM	Batch reactor	The reactor was a receptacle adjusted as Plexiglas of 3 L, provided with a porous circular stone and a hose connected to the tubes for the supply of compressed air. As effective volume of 0.3 L of bacterial suspension and 0.7 L of WCPM.	They used several functional groups and consortiums of bacteria. The systems were operated under mesophilic conditions (27 ºC) and HRT of 144 h. The COD of feeding was 880 mg/L.	pH COD TSS VSS Alkalinity

Table 5. Methodology for aerobic treatment of WCPM

Researcher, year	Kind of WCP	Treatment systems	Characteristics of the experimental equipment	Operation conditions	Parameters evaluated
Gutiérrez *et al.* (2007)	WCPL WCPM and WCPH	Batch rectors	They placed four (4) reactors of 500 mL each one, containing 20 % of the useful volume of mesophilic granular sludge proceeding from a beer industry, and 80 % of effluent to treat. The reactors were immersed in a thermal bath that allowed controlling the temperature. The produced biogas was meter by water displacement.	Initially the reactors were loaded, for ten days, with D +glucose on an equivalent concentration in COD of 1500 mg/L and solution of nutrients, for a retention time (RT) of 24 hours. Later they added to three reactors WCPL, WCPM and WCPH with concentrations of 1200-1300 mgCOD/L, 857-960 mgCOD/L and 860-870 mgCOD/L, respectively. The fourth reactor worked with glucose (D+ glucose). To reach the thermophilic conditions (55ºC ± 1ºC) the temperature was increased from the mesophilic conditions (37ºC ± 1ºC) at the reason of 1ºC/day. The RT in all the cases was 24 hours.	pH COD TSS and VSS Alkalinity VFA Methane

Researcher, year	Kind of WCP	Treatment systems	Characteristics of the experimental equipment	Operation conditions	Parameters evaluated
Gutiérrez *et al.* (2009)	WCPM and WCPH	Batch reactors	They placed three (3) reactors of 500 mL each one, containing 20 % of the useful volume mesophilic granular sludge proceeding from a beer industry, and 80 % of effluent to treat. The reactors were immersed in a thermal bath that allowed controlling the temperature. The produced biogas was meter by water displacement.	Initially the reactors were loaded, for ten days, with D +glucose on an equivalent concentration in COD of 1500 mg/L and solution of nutrients, for a retention time (RT) of 24 hours. Later they added to two reactors WCPM and WCPH with concentrations of 1876.9 and 1029.0 mgCOD/L, respectively. The third reactor worked with glucose (D+glucose). To reach the thermophilic conditions (55ºC ± 1ºC) the temperature was increased from the mesophilic conditions (37ºC ± 1ºC) at the reason of 1ºC/day. The RT in all the cases was 24 hours.	pH COD TSS and VSS Alkalinity VFA Methane
Rincón *et al.* (2002)	WCPL	UASB reactors	There were employed at a UASB reactor of 4 L, 0.098 m of diameter, 0.67 m high and 0.53 m high of water, inoculated with 30 % of granular sludge from a UASB reactor that treats residual waters of a brewery of the locality.	Initially, the reactor was fed with residual synthetic water that was containing glucose as the only source of carbon (1 g/L) and nutrients. Later, it was operated for 275 days with HRT from 38 to 5 h. The reactors were evaluated for organic loads of 0.78; 1.20; 1.46; 1.64; 1.90; 3.17 and 4.70 kg COD/m^{3}d for HRT of 36, 24, 21, 17, 11, 8 and 6 hours, respectively. They worked under mesophilic conditions (37ºC ± 1ºC).	pH Alkalinity COD Phenols
Díaz *et al.* (2005a)	WCPL WCPM WCPH	UASB reactors	They worked with 3 UASB reactors of 4 L, inoculated with 1.2 L of granular sludge from an UASB reactor treating residual waters of a brewery of the locality.	Initially, the reactor was fed with residual synthetic water that was containing glucose as the only source of carbon (850 mg/L) and nutrients. Later, the reactors UASB-1, UASB-2 and UASB-3 were fed by WCPL, WCPM and WCPH why organic loads of 1.06; 0.78 and 0.31 kg COD/m^{3}d, respectively. They worked under mesophilic conditions (37ºC ± 1ºC) during 1 month with HRT of 24 h.	pH Alkalinity COD SARA

Researcher, year	Kind of WCP	Treatment systems	Characteristics of the experimental equipment	Operation conditions	Parameters evaluated
Gutiérrez *et al.* (2006)	WCPL	UASB reactors	They used two UASB reactors constructed in Plexiglas with volumes of 1.7 and 2.5 L, operating under temperatures of 37 ± 1ºC and 55 ± 1°C, respectively. The reactors were provided with a jacket, supporting the temperature for recirculation of warm water. Both reactors were inoculated with mesophilic anaerobic granular sludge (20 % of the useful volume) proceeding from a beer industry.	Initially the reactors were load, for two days, with D+glucose on an equivalent concentration in COD of 1500 mg/L and solution of nutrients and TRH of 24 h; then WCPL was added. Later to reach the thermophilic conditions (55ºC ± 1ºC) in the thermophilic reactor, the temperature was increased from the mesophilic condition (37ºC ± 1ºC) to a rate of 1ºC/day. The reactors were evaluated for organic loads of 1.4, 1.9, 2.8 and 5.6 kg COD/m^{3}d and RTH of 24, 18, 12 and 6 hours, respectively.	pH Alkalinity COD VFA Methane Enzymes
Caldera *et al.* (2007)	WCPL	UASB reactor	They used a UASB reactor constructed in Plexiglas with volume of 2.5 L, inoculated with anaerobic mesophlic granular sludge (30 % of the useful volume) proceeding from a beer industry. The reactor was provided with a jacket, supporting the temperature of 55 ± 1°C for recirculation of warm water.	Initially the reactor was loaded, for two days, with D+glucose on an equivalent concentration in COD of 1500 mg/L and solution of nutrients, and HRT of 24 h; then WCPL was added. Later to reach the thermophilic condition (55ºC ± 1ºC), in the thermophilic reactor, the temperature was increased from the mesophilic condition (37ºC ± 1ºC) to a rate of 1ºC/day. The reactor was evaluated for 42 days, with HRT of 24 and 12 and organic loads of 1.4 and 2.8 kg COD/m^{3}d, respectively.	pH Alkalinity COD VFA Methane
Rincón *et al.* (2008)	WCPL WCPM	UASB reactors	They used two UASB reactors of 2.5 L, inoculated with 0.75 L of granular sludge from an UASB reactor treating residual waters of a brewery of the locality.	Initially, the reactors were fed with residual synthetic water that was containing glucose as the only source of carbon (850 mg/L) and nutrients. Later, the reactors UASB-1 and UASB-2 were fed with WCPL and WCPM APPL and organic load of 1.06 and 0.78 kg COD/m^{3}d respectively. They worked mesophilic conditions (37ºC ± 1ºC) during 1 month with HRT of 24 h.	pH Alkalinity COD SARA

Table 6. Methodology for anaerobic treatment of WCP

Researcher, year	Kind of WCP	Treatment systems	Characteristics of the experimental equipment	Operation conditions	Parameters evaluated
Rojas *et al.* (2008)	WCPC (WCPM and WCPH)	Coagulation and DAF	The DAF, consisted of a pressurization cell or saturation camera, constructed in material of transparent plastic of 90 mm of external diameter and 270 mm high. Inside the camera was finding a manual agitator of stainless steel and a filter that worked as diffuser; in addition, a series of connections and valves of the distribution and pressure of the water and air.	They worked with pressures of 30, 40 and 50 psi and recycle of 30%, 40% and 50%, and temperature of 25ºC. They evaluated a cationic flocculants of high molecular weight, in concentration of 0.006 % in volume (3.54 mg/L)	TSS Turbidity O&G
Caldera *et al.* (2009)	WCPH	Coagulation-flocculation	They used a Jar Test model JLT6; adding 1 L of WCP, to each of six precipitation jar of 1000 mL, taking one of these as a control.	They simulated coagulation, flocculation, and sedimentation processes to 100 rpm for rapid agitation for 1 minute and 30 rpm for slow agitation by 20 minutes. The sedimentation was 30 minutes. The initial turbidity of the water was 140 NTU. They used as coagulant commercial chitosan (CCH) (Sigma Chemical Co.) and chitosan obtained in the laboratory (LCH) to 100 ºC dissolved in acetic acid 0.10 M, preparing solutions of 0.6 %. They worked with concentrations of 24, 30, 36, 42 and 48 mg/L of solution of LCH and CCH, respectively.	pH COD TSS VSS Turbidity Color O&G Hydrocarbons
Caldera *et al.* (2011)	WCPH	Coagulation-flocculation	They used a Jar Test model JLT6; adding 1 L of WCP, to each of six precipitation jar of 1000 mL, taking one of these as a control.	They simulated coagulation, flocculation and sedimentation processes to 100 rpm for rapid agitation for 2 minutes, and 100 rpm for slow agitation for 30 minutes. The sedimentation was 30 minutes. The turbidity initial was 52 NTU. As coagulant agent was used commercial chitosan (CCH) dissolved in acetic acid 0.10 M, preparing solutions of 1.0%. The concentrations evaluated were 40,	pH COD TSS VSS Turbidity Color O&G Hydrocarbons

Researcher, year	Kind of WCP	Treatment systems	Characteristics of the experimental equipment	Operation conditions	Parameters evaluated
				42, 44, 46 and 48 mg/L of CCH solution.	

Table 7. Methodology for physicochemical treatment of WCP

Researcher year	Kind of WCP	Treatment systems	Characteristics of the experimental equipment	Operation conditions	Parameters evaluated
Rincón *et al.* (2004)	WCPL WCPC	UASB-SBR system	They used two types of reactors placed in series, a reactor UASB of 2.5 L of useful volume and a SBR. The reactor UASB was inoculated by sludge from an UASB reactor treating residual waters of a brewery. While the SBR reactor was inoculated with aerobic sludge from a wastewater treatment plant.	The system worked 195 days, in two stages. The first was feeding with WCPL from 1100 to 1230 mg COD/L (133 days) and the second one with WCPC of 176 and 264 mg COD/L (66 days). The effluent treated in the UASB was fed in the SBR. The HRT was 24 hours and the temperatures were UASB 37ºC and SBR 28 ºC.	pH Alkalinity COD Hydrocarbons Phenols
Paz *et al.* (2012)	WCPC	Superficial constructed wetlands (SCWFF)	They used two superficial constructed wetlands of free flow (SCWFF) to pilot scale. The support material was gravel and soil, and aquatic emergent plants that counted of support of gravel and soil, and aquatic emergent plants (*Cyperus luzulae y Cyperus ligulari* – SCWFF I, y *Cyperuz feraz, Paspalum sp. y Typha dominguesis* – SCWFF II), and a control (C) without plants.	They placed 30 plants for each species. The depth of the support was 0.25 cm with 7 % of gravel and 93 % of soil, and a water layer of 0.05 m of water. The flow fed was 8 mL/min, with a HRT of 7 days and organic load of 23.5 g COD/m^{2}d. The samples were collected weekly for 80 days.	COD pH Sulphide Phenols TSS VSS DO
Blanco *et al.* (2008)	WCPC	Sub-superficial constructed wetlands (SSCW)	The system SSCW consisted of three polyethelene tray of 1.28 m long for 0.45 m wide and 0.45 m high, one that of them as control (without plants) and the others two with emergent aquatic plants *Cyperus luzulae, Cyperus feraz L.C, Cyperus ligularis L.* y *Typha dominguensis* (SSCW I y SSCW II). The beds of the tray were constituted by 86400 cm^3 of gravel as support and a water level of 1.5 L to simulate a natural system of wetland.	The systems worked to continue flow, without recirculation of the effluent with an organic load of 29.42 g/m^{2}d, a flow of 10 mL/min and HRT of 7 days.	pH Alkalinity COD VSS Hydrocarbons Phenols

Table 8. Methodology for combined treatment of WCP

Researcher year	Treatment systems / WCP	COD (%)	TSS (%)	VSS (%)	Hydro-carbons (%)	O&G (%)	Phenols (%)	Turbidity (%)	pH	Alkalinity ($mgCaCO_3/L$)
Rojas et al. (2008)	Coagulation and DAF WCPC	__	77	__	__	90	__	69	__	__
Caldera et al. (2009)	Coagulation-flocculation WCPH	50.7	__	__	70.1	__	__	90.7	8.0-8.2	__
Caldera et al. (2011)	Coagulation-flocculation WCPH	12.5	55-61	41-63	70-90	39-59	__	76-78	7.9	__
Behling et al. (2003)	RBC WCPC	76.1	< 4	< 3	__	__	__	__	8.9	2343
Díaz et al. (2005a)	SBR WCPL, WCPM and WCPH	88.8 65.2 62.9	__	__	__	__	96.8 89.2 82.8	__	9.0-9.9 9.0-9.6 8.9-9.4	__
Díaz et al. (2005b)	SBR WCPM	65.1[a] 60.9[b]	__	__	76.8 79.5	55.5 62.4	87.5 92	__	__	__
González et al. (2008)	SBR WCPL and WCPH	88 66	__	__	84.4 73.8	__	95.6 79.4	__	__	__
Castro et al. (2008)	Batch reactor WCPM	62.4-89.8	63.3-9.5	__	__	__	__	__	7.4-6.6	__

a and b: different HRT

Table 9. Results of the treatment of WCP

Researcher year	Treatment systems / WCP	COD (%)	VSS (%)	Hydro-carbons (%)	Phenols (%)	pH	Alkalinity ($mgCaCO_3/L$)	SARA (%)	Methane content (%)
Gutiérrez et al. (2007)	Batch reactors WCPL, WCPM and WCPH	70.7 59.9 62.1	__	__		7.6 7.6 7.2	2673.7 2620.0 936.7	__	73.1 51.9 54.1
Gutiérrez et al. (2009)	Batch reactors WCPM and WCPH	68.2-69.2 55.9-50.4	__	__		8.2 7.5	__	__	__

Rincón et al. (2002)	UASB WCPL	23.8-86.1	__	__	10-59	7.6-8.0	2500-2800		24-95
Díaz et al. (2005a)	UASB WCPL, WCPM and WCPH	81.7 23.5 35.7	__	__	55.1 74.7 92.5	7.3-8.6 7.1-8.5 7.2-8.4	__	__	__
Gutiérrez et al. (2006)	UASB WCPL	40-80[M] 67-84[T]	42-73 52-67	__	__	7.4-8.5 7.9-8.0	1960-2633 2190-2454	__	53-79 54-80
Caldera et al. (2007)	UASB WCPL	78[a] 77[b]	__	__	__	8.0 8.2	2413 2945		87 77
Rincón et al. (2008)	UASB WCPL and WCPM	93 26	__	__	__	7.5 7.8	1955 2520	84 54	__
Rincón et al. (2004)	UASB-SBR WCPL-WCPC	95 79	__	74 82	99.9 90	9 9	2468 2405	__	__
Paz *et al.* (2012)	Superficial constructed wetlands WCPC	-	-		64.3 61.3	9.13-10.5 8.84-9.93	-	-	-
Blanco et al. (2008)	Sub-superficial constructed wetlands WCPC	31.4-65.7	45.2-91.9	77.5	94.7	8.9	2508	__	__

M: Mesophilic T: Thermophilic; a and b : different HRT

Table 10. Results of the treatment of WCP

2.4. Biological treatment of the waters associated with light crude oil production

The waters associated with the production of light crude oil (WCPL) are biodegradable in aerobic biological treatments, in anaerobic biological treatments and in a combination of these treatments. Díaz *et al.* (2005a) report that the COD removal in SBR was 88.8%, and the removal of phenols was 96.8%.

Likewise, the WCPL showed be biodegradable in anaerobic conditions in batch and continuous systems, under mesophilic conditions (37ºC) and thermophilic conditions (55ºC). In batch systems the COD removal reached 70.7% under mesophilic conditions (Gutiérrez *et al.*, 2007), while in UASB reactors under both temperature conditions, the efficiency of COD removal reached over 75%.

In UASB reactors the HRT influenced in the COD removal; so, Rincón *et al.* (2002) reported that under mesophilic conditions the optimal HRT was between 15 and 10 hours, with COD removal above 80%, but for HRT under 10 hours the system did not allow the methanogenic microorganisms to be able to transform volatile fatty acid (VFA), provoking the inhibition of the system. On the other hand, Gutiérrez *et al.* (2006) indicated that for the same temperature conditions, the HRT optimal was 18 hours with COD removal of 80%; they indicate also that for thermophilic conditions, the optimal HRT was 18 hours with COD removal of 84%, maintaining good COD efficient removal for HRT of 6 hours (67%).

When the efficiency of COD removal of WCPL in UASB reactors under mesophilic and thermophilic conditions were compared, major percentages of COD removal under thermophilic conditions for HRT under at 15 hours were observed. This removal of COD can be associated to high temperature accelerate the enzymatic biological systems. Nevertheless, there were not significant differences ($p>0.05$) between the values obtained for mesophilic and thermophilic temperature conditions, for the HRT from 12 to 24 hours.

When combined systems were used, the COD removal of the system was higher than those obtained in each separated system (Rincón *et al.*, 2004).

The maximum COD removal reached for the systems applied to WCPL were between 67% and 95%. In this aspect, the petroleum industry has alternatives to treat the WCPL; however, the final decision will be an economic decision between the temperature, the size of the reactor and energy costs. In the case of thermophilical route, it is necessary to considerate the cost of raising the temperature of the water, because the WCPL is at atmospheric conditions. For aerobic processes, the costs of the energy associated must be considered.

2.5. Biological treatment of the waters associated with medium crude oil production

It is observed in the Table 9 and Table 10 that the WCPM presented lower biodegradability than WCPL, for both aerobic and anaerobic systems. In discontinuous batch aerobic systems, Castro *et al.* (2008) report that the COD removal was between 62.4% and 89.8%; while for SBR reactors was between 60.9% and 65.2% (Díaz *et al.*, 2005 a; Díaz *et al.*, 2005b). On the other hand, in batch anaerobic reactors under thermophilic conditions, the COD removal was between 59.9% and 69.2% (Gutiérrez *et al.* 2007; Gutiérrez *et al.*, 2009). In UASB reactors, the COD removal was between 23.5% (Díaz *et al.*,2005a) and 26% (Rincón *et al.*, 2008).

In the different treatment systems it is observed that the COD removal for WCPM was between 23.5% and 89.8%.

2.6. Biological treatment of the waters associated with heavy crude oil production

In the case of the waters associated with heavy crude oil production (WCPH), the behavior was similar to WCPM. In SBR systems the COD removal was between 62.9% (Díaz *et al.*, 2005a) and 66% (González *et al.*, 2007). While in anaerobic batch reactor systems under thermophilic conditions, the COD removal was between 50.4% and 62.1% (Gutiérrez *et al.*, 2007; Gutiérrez *et al.*, 2009). On the other hand, in UASB reactors under mesophilic conditions, the COD removals were lower than 40% (Díaz *et al.*, 2005a; Rincón *et al.*, 2008).

2.7. Biological treatment of the combination of waters associated with crude oil production

The WCPC represent the combination of the waters in contact with different fractions of crude oil, whether produced in plant or by the researchers. The biodegradability of these waters has been studied in RBC and combined systems UASB-SBR (Table 8).

Behling *et al.* (2003) commented that the COD removal in RBC system used to treat WCPC was 76.1%, while Rincón *et al.* (2004) studied a UASB-SBR system and reported that the COD removal reached 79%, indicating that was important removals of phenols and hydrocarbons were obtained.

3. Discussion

Comparing the biodegradability of WCPL, WCPM and WCPH, it is observed that the WCPL present the major biodegradability in the different treatment systems and operating conditions studied.

The biodegradability of the WCP has been associated to diverse factors as SARA composition, phenols concentration, alkalinity, organic load, metals concentration and temperature.

Some researchers (Rincón *et al.,* 2002; Gutiérrez *et al.,* 2006; Gutiérrez *et al.,* 20007) argue that the WCPL biodegradability is good in anaerobic systems under mesophilic conditions and under thermophilic conditions. The final decision between the temperature used and size of the reactor will be economical, because the WCPL are at atmospheric temperature and the termophilic route implicates to consider the costs associated of warming the water. In the cases of WCPM and WCPH the studies realized up to the moment are not conclusive.

Other researchers (Gutiérrez *et al.,* 2007; Gutiérrez *et al.,* 2001; Gutiérrez *et al.,* 2012) share that the biodegradability of WCP is associated to the SARA composition present in these waters, as product of the contact with the crude oil associated. The difference of composition of these fractions confer characteristics that influence in their biodegradability, because the SARA fractions change in relation to the crude oil that is in contact with the WCP, being the WCPL the waters with the biggest percentages of saturated, considered more biodegradable than WCPM and WCPH.

When the organic fractions present in the WCP are compared, it is observed that WCPM and WCPH present a similar content of organic fractions ($p>0.05$). The opposite case was observed with the WCPL, which organic fractions are different in saturated, aromatics and resins, in comparing to WCPM and WCPH ($p>0.05$).

On the other hand, there is a tendency to increase the saturated fractions in WCP ($r=0.871$) with the increase of the API gravity of the crude oil with the water associated, following the order WCPL>WCPM>WCPH. In relation to the resins, it was observed that it increases with regard to the decrease of the API gravity of the crude oil with the WCP were associated following the order WCPL<WCPM<WCPH.

A study realized by Díaz *et al.* (2007) with WCPM from other tank farm of the Venezuelan petroleum industry, indicated that the SARA fractions can be removed from the WCP using UASB reactors. They obtained removals of 72% of saturated, 91% of resins and 71% of asphaltenes, and did not obtain removals of aromatics. They associated these results with the increases of the aromatic fractions for degradation of the fractions like resins and asphaltenes to aromatics.

Also the researchers have presented biodegradability percentages of different types of WCP under anaerobic conditions. They report values for mesophilic and thermophilic anaerobic systems of 80% and 78%, 45% and 86%, and 20% and 0%, for WCPL, WCPM and WCPP respectively in batch reactors (Gutiérrez and Caldera, 2011; Gutiérrez *et al.*, 2007; Rincón *et al.*, 2006).

In regard to phenols concentration, the studies mention that the consortium of microorganisms developed in mesophilic UASB reactors were influenced by the initial phenols concentrations, indicating that the phenols removal might be associated with the presence of different phenols compounds in the different types of WCP, with varied resistance to degradation and metabolism (aerobic/anaerobic).

Additionally, the studies indicate that the alkalinity values in the WCP were between 900 and 3000 mg $CaCO_3$/L. It has been commented that the difference of COD removal might be due to the acidity-basicity conditions in the WCP. The WCPH presented lower values of alkalinity (642.9-580.4 mg $CaCO_3$/L) and lower COD removal than WCPM. The alkalinity of WCPM was superior to 2000 mg $CaCO_3$/L. As for the pH, the WCP presented basic pH (7-10) for the different treatments.

In other cases, it is mentioned that the presence of metals in the WCP makes the treatment more complex. However, the metals K, Na, Fe, Cr, Pb and Zn can be used by thermophilic microorganisms or can be removed from the WCP and reach to the sludge by diverse mechanisms (Gutiérrez *et al.*, 2009).

In relation to degrading microorganisms present in the WCP, some have been isolated, and identified the genus *Aeromonas, Klebsielle, Xanthomona, Bacteroides* and *Acinetobacter*, as well as a consortium of them, that resulted to be effective in COD decrease (Castro *et al.,* 2008).

The Table 7 shows that WCP has been treated by coagulation-flocculation at laboratory level using chitosane as a coagulating agent in concentrations of 24 to 38 mg/L of solution of commercial chitosane (CCH), and by dissolved air flotation (DAF) using a cationic flocculants of high molecular weight.

Rojas *et al.* (2008) reported that the TSS removal and the turbidity in the WCPC were 77% and 69% respectively. On the other hand, Caldera *et al.* (2009, 2011) commented that the turbidity removal in the WCPH was 90.7%, accompanied of COD removal of 50.7%. In any case, the hydrocarbons removal and oils removal by physicochemical methods were between 70% and 90%, concluding that the cationic polymers represent an alternative to remove oily compounds in the WCP.

Table 8 shows other alternatives applied to treat WCP. In constructed sub-superficial wetlands COD removal of WCPC was between 31.4% and 65.7%, while in constructed superficial wetlands there was no COD removal. Both systems showed efficiency to remove more than 60% of the hydrocarbons present in the WCPC (Paz *et al.*, 2012; Blanco *et al.*, 2008).

The application of ozone also has been proposed to increase the biodegradability of the WCP. According to Gutiérrez *et al.* (2002), the application of ozone improves considerably the biodegradability of the WCP, with an increase of up to 87%. They concluded that the application of doses of ozone to WCP in the order of 30 mg/L of ozone, would affect favorably in the later biological processes applied.

4. Conclusions

The WCP from the different cuts: light (WCPL), medium (WCPM), heavy (WCPH) and combinations of them (WCPC), have different characteristics and their biodegradability or treatment are associated on the SARA compositions, organic matters concentration, hydrocarbons and phenols concentrations, and the operation conditions (HRT and temperature).

The biodegradability of the WCP followed the order WCPL>WCPM>WCPH.

The COD removal in biological systems changed between 67%-95%, 23.5%-89.8% and 35%-66% for WCPL, WCPM and WCPH, respectively.

The physicochemical treatment DAF and coagulation, removed hydrocarbons and oils between 70% and 90%.

Other parameters like phenols, hydrocarbons and SARA fractions, can be removed from the WCP by biological treatments.

It is necessary to analyze other parameters and operating conditions, as well as to conduct an economic evaluation before the treatment selection.

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