Biodegradation

Science and Technology

William Chang

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Edited by **William Chang**

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Preface

This book aims to highlight the current researches and provides a platform to further the scope of innovations in this area. This book is a product of the combined efforts of many researchers and scientists, after going through thorough studies and analysis from different parts of the world. The objective of this book is to provide the readers with the latest information of the field.

This book presents an array of various research works discussing different technologies that have been used for the escalation of biodegradation process. The book deals with various factors and aspects of biodegradation. These include hydrocarbons biodegradation, and biodegradation and anaerobic digestion.

I would like to express my sincere thanks to the authors for their dedicated efforts in the completion of this book. I acknowledge the efforts of the publisher for providing constant support. Lastly, I would like to thank my family for their support in all academic endeavors.

Editor

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Biodegradation of Hydrocarbons

Chapter 1

Biodegradability of Water from Crude Oil Production

Edixon Gutiérrez and Yaxcelys Caldera

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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.

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.

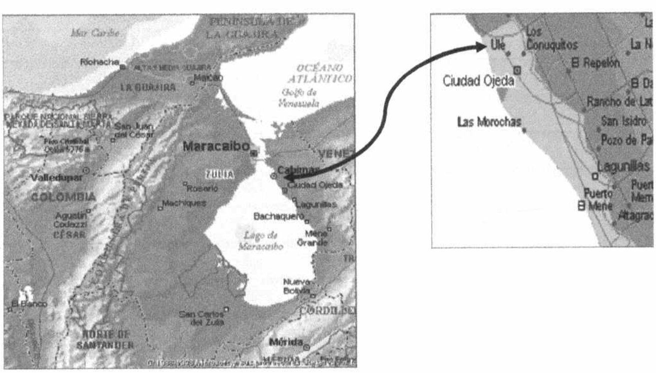

Figure 1. Geographical location of the Ulé tank farm, Tía Juana Zulia state, Venezuela.

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