


EREM 74/4 Journal of Environmental Research, Engineering and Management Vol. 74 / No. 4 / 2018 pp. 66-78 DOI 10.5755/j01.erem.74.4.21428 © Kaunas University of Technology	A Comparative Review and Multi-criteria Analysis of Petroleum Refinery Wastewater Treatment Technologies	
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A Comparative Review and Multi-criteria Analysis of Petroleum Refinery Wastewater Treatment Technologies

Taylor Livingston, Bassim Abbassi

School of Engineering, University of Guelph, 50 Stone Rd E, Guelph ON, N1G 2W1, Canada

Corresponding author: babbassi@uoguelph.ca

Bassim Abbassi, School of Engineering, University of Guelph, 50 Stone Rd E, Guelph ON, N1G 2W1, Canada

The global economy's continued dependence on fossil fuels is associated with a multitude of environmental concerns, including the production of hazardous wastes in petroleum refineries. Large quantities of petroleum refinery wastewater (PRWW) are produced daily, requiring the development of appropriate treatment methods. Activated sludge biological treatment is commonly used to treat PRWW; however, this treatment method has a high sludge production, high operational time and may not be optimally suited for the variable loading conditions of refineries. Multi-criteria analysis (MCA) is a tool capable of evaluating different wastewater treatment technologies through the weighted consideration of multiple environmental and economic factors. The following methods of treating PRWW were reviewed and evaluated using a multi-criteria analysis: biodegradation, advanced oxidation processes, electrocoagulation and microbial fuel cell technology. The MCA considered removal efficiencies, sludge production, cost-benefit, process complexity and operational time of each method and was conducted under six different weighting scenarios. Advanced oxidation processes were preferred by this analysis under all six scenarios, with overall index scores (OIS) ranging from 7.84 to 8.51 out of a possible 10 points. Biodegradation of PRWW obtained was found to have the greatest overall removal efficiencies; however, the high operational time and sludge production of this method resulted in a maximum OIS of 7.59. Electrical methods, such as electrocoagulation and microbial fuel cell technology, required further improvements in removal efficiencies to be considered as a standalone treatment method. Further research into all methods, particularly microbial fuel cell technology, is recommended.

Keywords: petroleum refinery, wastewater, hazardous waste, multi-criteria analysis.

Introduction

The global economy's continued reliance on fossil fuels is linked to multiple environmental concerns (Greenshields et al., 1987). Petroleum refineries convert crude oil into gasoline and other petroleum-based products, such as asphalts, diesel and lubricating oils. Efficiency is inherently a priority in this industrial process, with refineries operating continuously and employing a variety of processes to produce the desired end products. Refineries first separate crude oil into its different constituent products through distillation by boiling point, a process called fractional distillation (Kockmann, 2017). Each constituent may then be subjected to a series of processes to maximise value of the finished products, including the conversion of the size or shape of hydrocarbons, solvent extraction of aromatic compounds and pyrolysis cracking to produce synthetic organic compounds (Greenshields et al., 1987). Sulphur and nitrogen may be removed by stripping the liquid and the gases or liquids produced may be washed or scrubbed to remove hydrogen sulphide, mercaptans, phenols, cresols and naphthenic acids. Wastewater produced in petroleum refineries consists of cooling water and the wastewater from these industrial processes, which may contain inorganics, oil, ammonia, sulphides, mercaptans, phenols and hydrocarbons, with the highest contaminant levels found in wastewater from fluid catalytic cracking units, crude desalting units, coking units and condensers (Burks and Wagner, 1983; Greenshields et al., 1987; Li et al., 2015).

Although several refineries employ wastewater reuse processes where possible, such as the use of wastewaters from fluid catalytic cracking processes for desalting processes, complete reuse of wastewater is currently not a viable option (Burks and Wagner, 1983). The current treatment of petroleum refinery wastewater (PRWW) typically involves gravitational oil-water separation, air flotation for suspended matter removal, and activated sludge biological treatment (El-Naas et al., 2016; Li et al., 2015; Pajoumshariati et al., 2017; Wang et al., 2015). While biological treatment is typically sufficient in reducing the high concentrations of organics, the high chemical oxygen demand (COD) and high concentrations of sulphides and other

contaminants present challenges for the viability of biological treatment alone (El-Naas et al., 2016; Mallick and Chakraborty, 2017). Furthermore, the variable loading conditions that are characteristic of petroleum refineries present the risk of introducing sudden, inhibitory conditions that are not conducive to successful biological degradation (Pajoumshariati et al., 2017).

The production of sludge through biological treatment of PRWW presents a further disposal problem. Schedule 1, section F of Ontario's Regulation 347 for hazardous industrial waste from non-specific sources sets limits for the content of contaminants in sludge produced through the treatment of petroleum refinery wastewater. The list of compounds that render petroleum refinery sludge as a hazardous waste product in Ontario include benzene, ethylbenzene, phenol, toluene and xylene (Government of Ontario, 2017a). Although the treatment of sludge from petroleum refineries represents a major environmental concern, this paper focuses on the treatment of PRWW.

Multiple PRWW treatment technologies are currently being studied, including biodegradation (Banerjee and Ghoshal, 2016), advanced oxidation processes (AOP) (Chen et al., 2014), electrocoagulation (Abdelwahab et al., 2009) and microbial fuel cell (MFC) technology (Guo et al., 2015). A comparative assessment of these PRWW treatment technologies requires the consideration of multiple environmental and economic factors. Multi-criteria analysis (MCA) is a decision-making tool which condenses a set of ranked criteria into an overall index score (OIS), allowing for comparative analysis of a set of alternatives (Plakas et al., 2016). The MCA has been used to differentiate between elements of wastewater treatment plant design (Benedetti et al., 2010) as well as between household (Jóźwiakowski et al., 2015), winery (Zorpas and Saranti, 2016) and tertiary wastewater treatment technologies (Plakas et al., 2016). The use of multiple scenarios which attribute different weightings for each parameter may be used to strengthen the analysis and allow for better interpretation of the results (Jóźwiakowski et al., 2015). Therefore, the MCA is considered a suitable approach to evaluate between different methods of treating PRWW. The objective of this study was to examine

different methods of treating PRWW and conduct the MCA to assess each for their viability as an appropriate PRWW treatment technology.

Methods

Review of PRWW treatment methods

A review of governmental regulations pertaining to PRWW effluent in Ontario, Canada, was conducted to aid in the identification of parameters for consideration in the MCA. The five parameters selected for consideration in the MCA were removal efficiencies, sludge production, costs and benefits associated with energy usage, process complexity and operational time.

Several recent studies using each of biodegradation, AOP, electrocoagulation and MFC to treat PRWW were reviewed with respect to the parameters set out in the MCA. For each treatment technology, an averaged value for each MCA category was calculated or discussed using the best operating conditions from each experiment. The arithmetic mean and standard deviation for each parameter were determined to provide an estimation of the overall efficiency of each treatment method for use in later analysis.

Multi-criteria analysis

For each treatment technology, a ranking index was determined using the information and values described during the review section for that technology. The methodology used to determine the ranking

indices varied between categories. They are summarised in Table 1.

Within the removal efficiency category, the removal efficiencies for COD, phenols, sulphides and oil and grease were given an equal weighting of 25%. Similarly, the cost-benefit category was subdivided to consider energy production (weighted at 20%) and energy consumption (weighted at 80%).

Weighting factors and qualitative ranked scores were determined by the authors based on previous expertise. An overall index score for each method was determined using an adapted version of the methods set out by Józwiakowski et al. (2015) and Plakas et al. (2016), as described by Equation 1 and the best technology was selected using Equation 2.

$$OIS = \sum_{j=1}^M \sum_{i=1}^N r_{ij} * f_i * c_j \quad (1)$$

Where: r – ranking indices for each feature; f – feature weighting factor; N – number of features within each category; c – category weighting factor; M – number of categories; OIS – overall index score.

$$BT = MAX(OIS_n) \quad (2)$$

Where: BT – best technology; n – treatment technology (1, 2, 3, 4).

To strengthen the results of this analysis, the MCA was conducted under six scenarios which varied the weighting factors for each category. Fig. 1 details the process used to conduct the multi-criteria analysis.

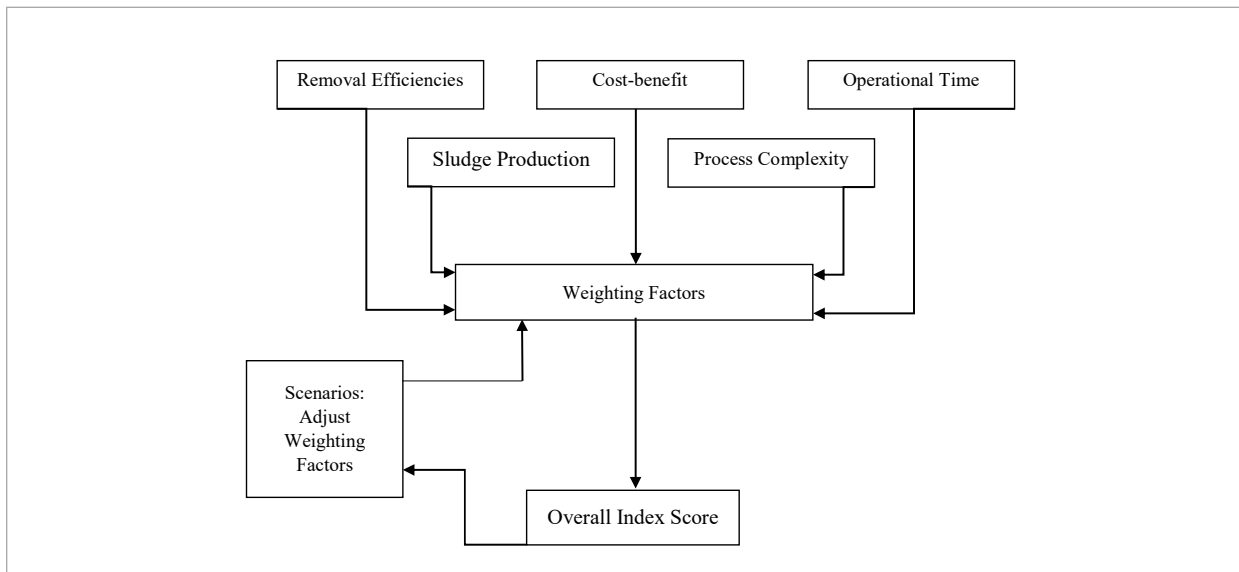
Table 1

Categories considered in the MCA and methods used to determine ranking indices

Category	Type	Objective	Determination of Ranking Index
1	2	3	4
Removal efficiencies	Quantitative	Maximisation	Percentages divided by 10
Sludge production	Qualitative	Minimisation	Ordered by performance and given a score of 1, 4, 4, 10
Costs and benefits	Qualitative	Maximisation/ Minimisation	Energy production: given either 0 or 10; Energy consumption: ordered by performance and given a score of 1, 1, 7, 10
Process complexity	Qualitative	Minimisation	Ordered by performance and given a score of 1, 4, 7, 10
Operational time	Quantitative	Minimisation	Divided by the maximum time, expressed out of 10

Fig. 1

Overview of the multi-criteria analysis with weighting scenarios



The ranking indices for each category as determined in the review sections remained constant throughout the analysis. Six weighting scenarios giving different levels of consideration to each category were used in this analysis, allowing for the calculation of six OISs for each technology using Equation 1. The OISs for each technology could then be directly compared, with the best technology being selected as that with the greatest OIS, as shown in Equation 2.

Results and Discussion

Review of PRWW regulations: case study in Ontario

To provide context to the importance of regulatory compliance for petroleum refineries, a case study of relevant regulations in Ontario was conducted. The estimation of current process water usage by petroleum refineries in Ontario provides an indicator of the total volumes of wastewater that require treatment and provides a sense of the scale needed for treatment within refineries. Table 1 provides a summary of the oil production rate and process water usage for five of Ontario's seven refineries, comparing past

rates from a 1987 study to current rates (Greenshields et al., 1987). Table 2 compares process water usage data for refineries for which comparative data were available in Ontario, Canada. Where the ownership of a refinery has changed, the former company is noted in brackets. Data for current process water usage were estimated using the correction factor in Equation 3.

$$WU_c = \frac{WU_p}{OP_p} \times OP_c \quad (3)$$

Where: WU_c – current process water usage; WU_p – previous process water usage; OP_p – previous oil production; OP_c – current oil production.

The results from this calculation for five Ontarian petroleum refineries are summarised in Table 2.

Table 2 provides an estimation that five petroleum refineries in Ontario currently produce a ratio of wastewater to oil production of 0.69, which is in agreement with the literature value of 0.4–1.6 (El-Naas et al., 2016; Wang et al., 2015). This wastewater contains several compounds that require monitoring and treatment to limit exposure of the environment and humans to these compounds. Ontario Regulation 537/93 provides a listing of the maximum daily and monthly

Table 2

Process water usage in Ontarian petroleum refineries, relative to oil production

Refinery	Previous Oil Production Rate [m ³ /day] (Greenshields et al., 1987)	Previous Process Water Usage [m ³ /day] (Greenshields et al., 1987)	Current Oil Production Rate [m ³ /day] (Government of Ontario, 2017b)	Current Process Water Usage [m ³ /day] (calculated)
1	2	3	4	5
Imperial Oil Ltd. Sarnia (Esso Petroleum)	19,078	18,000	19,900	18,776
Petro-Canada Lubricants Center	9,539	13,200	12,900	17,851
Petro-Canada (Oakville)	13,037	4,800	14,150	5,210
Novacor Chemicals Ltd. (Petrosar Ltd.)	15,899	6,580	14,600	6,042
Imperial Oil Ltd. Nanticoke (Texaco Canada)	17,489	6,810	18,600	7,243
Total [m ³ /day]	75,042	49,340	80,150	55,121

average loading for parameters of concern for each of Ontario's refineries (Government of Ontario, 2017b). Petroleum refineries are required to monitor process water and cooling water to ensure that contaminant levels adhere to regulations (Government of Ontario, 2017b).

At the federal level, the Government of Canada sets regulations regarding the maximum daily and monthly allowances for deleterious substances in petroleum refinery liquid effluent (Government of Canada, 2018). Section four of the Petroleum Refinery Liquid Effluent Regulations for Canada defines deleterious substances as oil and grease, phenols, sulphide, ammonia nitrogen, total suspended matter and any substance that could potentially alter the pH of water (Government of Canada, 2018). The list of deleterious substances aligns with the parameters of concern in the United States. An Environmental Protection Agency study examined removal rates for phenol, sulphide, ammonia, biological oxygen demand (BOD), total organic carbon (TOC) and oil and grease using different treatment technologies (Burks and Wagner, 1983).

For industry to ensure regulatory compliance, treatment methods must be capable of adequately reducing these hazardous substances. Where data existed, removal efficiencies for these substances were incorporated into the multi-criteria analysis.

Biodegradation

Biological treatment is commonly used in refineries to treat PRWW, following separation and flotation processes (Pajoumshariati et al., 2017). Therefore, current research into the biodegradation of PRWW is focused on optimising the design and operating conditions of bioreactors. A complication of biological treatment is the production of sludge, which is subject to regulation as a solid waste (Santo et al., 2013). Microbial populations require an adaptation period to adjust to their environment prior to degradation and can be quite sensitive to toxic loading conditions (Pajoumshariati et al., 2017). Despite this, PRWW is seen as a suitable substrate for biological treatment due to its high hydrocarbon content, which microorganisms can fully degrade under the right conditions (Mallick and Chakraborty, 2017). Biological treatment systems require an inoculation period where the reactor is inoculated with bacteria-containing sludge and are often dosed with nutrients throughout operation to maintain microbial populations (Mallick and Chakraborty, 2017). One important parameter for biological treatment is the hydraulic retention time (HRT), which is a measure of wastewater treatment time (Santo et al., 2013). The main biological treatment processes of PRWW include activated sludge systems, moving bed biofilm reactors, membrane sequencing batch

Table 3

Comparison of results from studies into biodegradation for PRWW treatment

Reference	Description	Hydraulic Retention Time [hours]	COD Removal [%]	Organics Removal [%]	Oil & Grease Removal [%]	Phenols Removal [%]	Sulfide Removal [%]	N-NH ₄ ⁺ Removal [%]
1	2	3	4	5	6	7	8	9
(Pajoumshariati et al., 2017)	Membrane sequencing batch reactor	8	80	81.5% TOC reduction; 93.4% TPH reduction	82			
(Schneider et al., 2011)	Moving bed biofilm reactor	6	69-89			89-99		45-86
(Mallick and Chakraborty, 2017)	Sequential anoxic-aerobic moving bed reactors; used synthetic PRWW	64	99.9	99.9% HC reduction		100	100	100
(Banerjee and Ghoshal, 2016)	Fluidised bed bioreactor	130	97.86			98.03		
(Santo et al., 2013)	Activated sludge system with recycling	20	95	87% TOC reduction				
Mean		46	90		82	97	100	83
Standard Deviation		53	10		-	3	-	24

reactors and fluidised bed reactors (Pajoumshariati et al., 2017; Santo et al., 2013; Schneider et al., 2011). The results from several studies which employed one of these forms of biological treatment on PRWW are summarised in Table 3.

The highest removal efficiencies were achieved at the highest HRTs, suggesting that longer contact time increases removal efficiency under any method of biological treatment. The best results were obtained using sequential anoxic-aerobic bioreactors, with nearly perfect removal efficiencies for all parameters (Mallick and Chakraborty, 2017). Overall removal efficiencies were quite high for biological treatment, although there are considerations of long operational times and high sludge production of biological treatment.

Advanced oxidation processes

Advanced oxidation processes (AOP) are a class of wastewater treatment processes that employ a combination of ultraviolet radiation, hydrogen peroxide, ozone, TiO₂ photo-catalysis, photo-ferrioxalate,

Fenton and photo-Fenton processes (Estrada-Arriaga et al., 2016). The Fenton process uses Fe²⁺, supplied by FeSO₄ and H₂O₂ to generate hydroxyl radicals, and the photo-Fenton process involves the addition of ultraviolet radiation (Yan et al., 2014). Photo-ferrioxalate reactions use ultraviolet radiation in combination with ferrioxalate (FeC₂O₄) (Estrada-Arriaga et al., 2016). These processes generate highly reactive hydroxyl radicals (•OH) which react with the organic contaminants of PRWW to trigger successive oxidative reactions until mineralisation of the contaminants is achieved (Davarnajad et al., 2015). Studies which used AOP to treat PRWW attempted to obtain the optimal ratio of reagents, duration and ultraviolet exposure. The results from these conditions are summarised below in Table 4.

Table 4 indicates that AOP treatment times are relatively low and that these reactions were tested under acidic conditions, with an average pH of 5. However, removal efficiencies for COD and oil and grease are low, in the range of 60–70%.

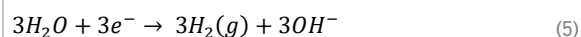
Table 4

Comparison of results from studies into AOP for PRWW treatment

Reference	Description	Time [min]	pH	COD Removal [%]	Organics Removal [%]	Oil & Grease Removal [%]	Phenols Removal [%]	Sulphide Removal [%]
1	2	3	4	5	6	7	8	9
(Chen et al., 2014)	Granulated activated carbon with manganese oxide and ozone	80	6.03	54.6	49.1% TOC reduction		71.2	
(Estrada-Arriaga et al., 2016)	Photo-ferrioxalate	120	5	84			100	93
(Bustillo-Lecompte et al., 2015)	Ultraviolet radiation, hydrogen peroxide	45	5.0		78.38% TOC reduction			
(Coelho et al., 2006)	Fenton followed by photo-Fenton reactions	120			85% DOC reduction	66		
(Aljuboury et al., 2015)	Fenton's reagent and photo-catalyst (TiO ₂)	90	4.18	48	64% TOC reduction			
Mean		91	5	62		66	86	93
Standard Deviation		31	1	19		-	20	-

Electrocoagulation

Electrocoagulation is a wastewater treatment technology that uses electrical oxidation of an anode through the application of current to generate metal hydroxides, which act as coagulants, capable of removing pollutants from PRWW (El-Naas et al., 2009). Newly formed metal hydroxides form flocs which remove contaminants by adsorbing soluble organics and can then be removed via sedimentation or flotation (Abdelwahab et al., 2009). The apparatus for electrocoagulation involves two electrodes, an anode and a cathode, which are connected to a circuit which supplies voltage to the system (Bhagawan et al., 2016). The anode is termed the sacrificial anode, as it is the source of metal ions in the solution (Bhagawan et al., 2016). The most commonly used anode and cathode material is aluminum, which was found to have the best removal efficiencies, compared with iron and stainless steel (El-Naas et al., 2009). The anodic and cathodic reactions for electrocoagulation using an aluminum anode are displayed below in Equations 4 and 5, respectively.



As shown in Equations 4 and 5, applied current causes the oxidation of the metal anode into metal ions, which then form metal hydroxides in the water (An et al., 2017). Concurrent reduction at the cathode produces hydrogen gas, which increases turbulence in the water, assisting with the flocculation of pollutants (El-Naas et al., 2009). Electrocoagulation produces sludge as pollutants precipitate out of the liquid, although typically in lower quantities than biological methods (Abdelwahab et al., 2009; Bhagawan et al., 2016). Increases in variables such as current density, the thickness of the anode, or the amount of metal supplied have been found to increase the removal of phenol from PRWW (Abdelwahab et al., 2009). A comparison of several studies which employed electrocoagulation to treat PRWW is summarised below in Table 5.

The operational time for this treatment technology was minimal, averaging 64 minutes. In general, removal efficiencies are acceptable, apart from COD and sulphide removals.

Table 5

Comparison of results from studies into electrocoagulation for PRWW treatment

Reference	Anode/Cathode Material	Time [min]	Current Density [mA/cm ²]	COD Removal [%]	Organics Removal [%]	Oil & Grease Removal [%]	Phenols Removal [%]	Sulfide Removal [%]	N-NH ₄ ⁺ Removal [%]
1	2	3	4	5	6	7	8	9	10
(Yan et al., 2014)	Graphite; addition of Fe, air and pH 3	60		89			64.20		99.5
(Abdelwahab et al., 2009)	Aluminum	120	23.6	0	3% BOD reduction		92		
(Bhagawan et al., 2016)	Aluminum	20	16.6	84	67% TOC reduction	84	89		
(El Naas et al., 2009) Lightly contaminated PRWW	Aluminum	60	13	63				93	
(El Naas et al., 2009) Heavily contaminated PRWW	Aluminum	60	13	42				24	
Mean		64	16.6	56		84	82	59	99.5
Standard Deviation		36	5.0	36		-	15	49	-

Microbial fuel cells

The application of microbial fuel cells to treat petroleum refinery wastewater represents a new area of research with the objective of capturing the chemical energy stored in wastewater contaminants (Guo et al., 2015). MFC are an advancement of biological treatment, using the oxidative power of bacteria to oxidise organic and inorganic compounds, whilst creating current (Logan et al., 2006). The electrons from oxidised compounds flow from the anode through a conductive material towards the cathode, which may be separated by an ion permeable membrane (Logan et al., 2006; Srikanth et al., 2016). Providing external potential between the anode and cathode promotes metabolic reactions by microorganisms, such as the production of hydrogen and degradation of waste compounds (Mohanakrishna et al., 2018). The counter flow of electrons through a conductive material generates electrical current (Logan et al., 2006; Srikanth et al., 2016). MFC as a wastewater treatment do not require aeration and produce less sludge compared with other methods (Zhang et al., 2014). MFC have been studied for the treatment of municipal

wastewaters and are currently being investigated as a potential technology to treat PRWW (Guo et al., 2015). Different configurations of MFC have been studied, with important design parameters including the electrode material, selection of single or double chamber design, the use of a proton-exchange membrane and the spacing between electrodes (Zhang et al., 2014). The simplest electrode materials are graphite and carbon cloth, while platinum catalysts can be incorporated to increase the rate of reduction reactions (Logan et al., 2006). The studies reviewed used a variety of designs, operated at the laboratory scale. Two indicators of the electrical output of a MFC are power density, a measurement of the power generated relative to the anode surface area, and coulombic efficiency, the ratio between the total coulombs transferred from the substrate to the anode and that which is theoretically possible (Logan et al., 2006). These parameters are included in Table 6 in addition to the removal efficiencies and operational time.

Table 6 demonstrates that MFC are capable of treating some of the hazardous compounds in PRWW. The low coulombic efficiency indicates that more studies

Table 6

Comparison of results from studies into MFC for PRWW treatment

Reference	Description	Time [hours]	Power Density [mW/m ²]	Coulombic Efficiency [%]	COD Removal [%]	Organics Removal [%]	Oil & Grease Removal [%]	Phenols Removal [%]	Sulphide Removal [%]
1	2	3	4	5	6	7	8	9	10
(Srikanth et al., 2016)	Continuous mode	16	225	2	84	99% HC reduction	95	52.3	79.5
(Zhang et al., 2014)	Spaced electrode assembly	-	255	6–11	84	92% HBOD reduction			
(Guo et al., 2015)	Double chamber; separated by proton-exchange membrane	50			47.1		65.5	75.5	87.7
(Mohanakrishna et al., 2018)	Single chamber	96	222.5		75.78	92% DRO reduction			35
Mean		54	234	5	73		80	63.9	67
Standard Deviation		40	18	5	18		21	16.4	28

are required for this technology to become a viable means of energy generation. The toxicity of PRWW to microorganisms makes PRWW a less desirable substrate for MFC treatment than municipal drinking water, which has been found capable of producing higher power densities (Zhang et al., 2014). However, there is potential for MFC to be used as a pre-treatment technology to improve the biodegradability of PRWW, while generating energy in the process (Guo et al., 2015). Although more research into this application is required, MFC offers a promising means of partially treating PRWW, with the added value of recovering energy from the wastewater.

Multi-criteria analysis

The averaged values and descriptors obtained through the previous treatment technology review sections enabled the development of ranking indices for the features of each technology, as summarised in Table 7. The calculated mean removal efficiencies that were used to determine the ranking indices for that category are intended to provide an overall estimation of the efficiency of each method for the purposes of this comparative review. Such values lack complete

accuracy due to the low number of data points and different methodologies used within each study.

The multi-criteria analysis calculations were conducted under six different weighting scenarios. The category weighting factors used in Equation 1 for removal efficiencies, sludge production and cost-benefit were varied in each scenario. The category weighting factors for process complexity and operational time were kept constant at 10% through all six scenarios as refinery operations generally have sufficiently great organisational capacity to render such considerations as minimal. A summary of the category weighting factors used in calculations under the six different weighting scenarios is provided in Table 8.

The multi-criteria analysis resulted in an OIS for each treatment technology for each of the six weighting scenarios set out in Table 8. The resulting OIS are presented in Fig. 2, where a maximum OIS of 10 points was possible in this analysis.

AOP received the highest overall index score for all six category weighting scenarios, ranging from 7.84 to 8.51. Although the greatest overall removal efficiencies were obtained by biodegradation, this treatment method ranked second, with a maximum overall index score

Table 7

Ranking indices for each technology for use in multi-criteria analysis calculations

Category	Feature	Treatment Technology			
		1	2	3	4
1	2	3	4	5	6
Removal efficiencies	COD	9.0	6.2	5.6	7.3
	Oil & Grease	8.2	6.6	8.4	8.0
	Phenols	9.7	8.6	8.2	6.4
	Sulphides	10.0	9.3	5.9	6.7
Sludge production	Sludge production	1	10	4	4
Cost-benefit	Energy requirement	10	7	1	1
	Energy production	0	0	0	10
Process complexity	Process complexity	10	7	4	1
Operational Time	Operational time	1.5	9.7	9.8	0

1 – biodegradation, 2 – AOP, 3 – electrocoagulation, 4 – MFC.

Table 8

Weighting factor given to each category under six weighting scenarios

Scenario	Removal Efficiencies	Sludge Production	Cost-benefit	Process Complexity	Operational Time
1	2	3	4	5	6
1	0.40	0.20	0.20	0.10	0.10
2	0.40	0.30	0.10	0.10	0.10
3	0.50	0.20	0.10	0.10	0.10
4	0.50	0.30	0.00	0.10	0.10
5	0.60	0.10	0.10	0.10	0.10
6	0.60	0.20	0.00	0.10	0.10

Fig. 2

Results of the multi-criteria analysis under six weighting scenarios

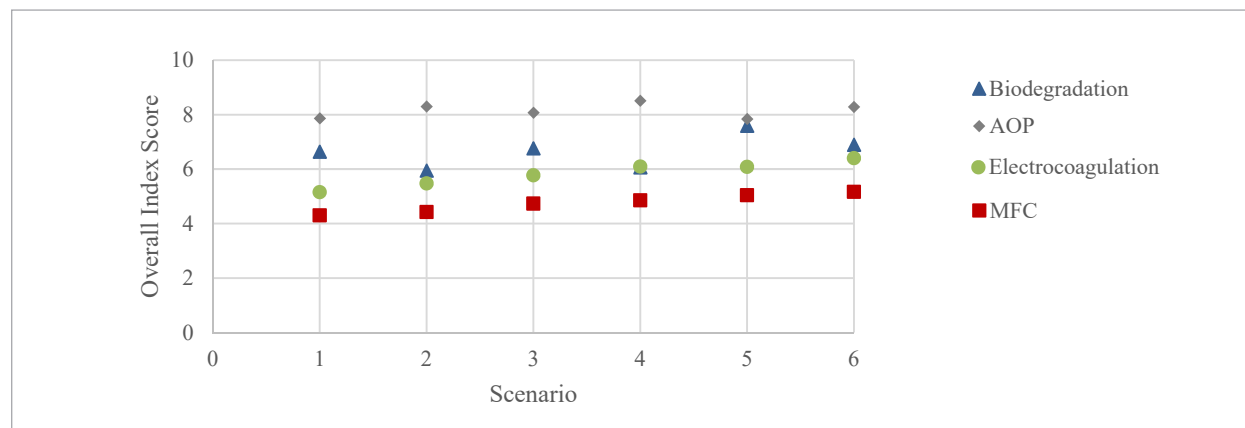


Table 9

Assessment of preferred treatment technology within each category considered by the MCA

Ratio of Category Weighting Factors (1:2:3:4:5)	Preferred Treatment Technology	Treatment Technologies Ordered from Highest to Lowest OIS
1	2	3
1:1:1:1:1	AOP	AOP, biodegradation, electrocoagulation, MFC
1:0:0:0:0	biodegradation	biodegradation, AOP, MFC, electrocoagulation
0:1:0:0:0	AOP	AOP, MFC/electrocoagulation, biodegradation
0:0:1:0:0	biodegradation	biodegradation, AOP, MFC, electrocoagulation
0:0:0:1:0	biodegradation	biodegradation, AOP, electrocoagulation, MFC
0:0:0:0:1	electrocoagulation	electrocoagulation, AOP, biodegradation, MFC

1 – removal efficiencies, 2 – sludge production, 3 – cost-benefit, 4 – process complexity, 5 – operational time.

of 7.59. This discrepancy may be attributed to the high retention time and sludge production associated with biological methods of treatment. Electrocoagulation and MFC received maximum overall index scores of 6.4 and 5.16, respectively. Table 9 provides insight into the determinations made by the multi-criteria analysis through examination of which treatment technologies performed the greatest within each of the categories.

As the results of Table 9 demonstrate, AOP received the highest OIS under every scenario because it performed well in every category considered by the MCA. Biological treatment technologies may be deemed the most suitable treatment technology for PRWW if only removal efficiencies were considered. However, the consideration of multiple criteria demonstrates that the low ranking indices for the undesirable characteristics of biodegradation, such as high operational time and sludge production make it the less preferable PRWW treatment technology compared with AOP.

Conclusions

The petroleum refinery industry requires research into new methods of treating refinery wastewater to ensure compliance with regulations. Four different methods of treating refinery wastewater were reviewed: biodegradation, AOP, electrocoagulation and

MFC. Each method of treatment was reviewed with respect to five categories: removal efficiencies, sludge production, energy requirements and production, process complexity and operational time. For each treatment method, each feature was given a ranking index and an overall index score was calculated using a multi-criteria analysis under six different weighting scenarios.

MCA with a scenario analysis proved to be a robust method to evaluate the relative merits of different PRWW treatment technologies. Through this assessment, AOP received the highest overall index scores for each of the six scenarios, up to a maximum of 8.51 out of 10. The greatest overall removal efficiencies were found for biodegradation; however, considerations of the high operational time and sludge production characteristic of biological treatment reduced the overall index score.

Opportunities exist within each treatment method for future research efforts to make improvements in sludge production, removal efficiencies or other parameters of concern. The application of MFC for PRWW treatment should be subject to further research, as concurrent energy production is a desirable co-benefit of treatment that may warrant further study. Further research to improve all methods of treatment is recommended to improve efficiencies of PRWW treatment for the petroleum refinery industry.

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