

Impact of biodiesel production on wastewater generation

Impacto da produção de biodiesel na geração de águas residuais

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ABSTRACT

Biodiesel production has intensified in recent years and the traditionally applied method for its production is homogeneous alkaline transesterification, with the formation of esters and glycerol, which need to be separated. Also, the crude biodiesel needs to be purified at the end of the reaction to remove the remaining catalyst, glycerol, soap, oil, and alcohol, which can impair engine performance. This process generates large quantities of wastewater that need to be properly disposed of to avoid polluting the environment. This article provides a review of the biodiesel production process and the need for a purification step, focusing on wastewater generation. Traditional and advanced methods for treating wastewater originating from biodiesel production are described and discussed. Details regarding patents published in the past 5 years, related to techniques for the treatment of these wastewaters, are also included.

Keywords: advanced treatments; biodiesel; conventional treatment; pollution; purification; wastewater.

RESUMO

A produção de *biodiesel* tem-se intensificado nos últimos anos e o método tradicionalmente aplicado para sua produção é a transesterificação alcalina homogênea, com a formação de ésteres e glicerol, que precisam ser separados. Além disso, o *biodiesel* bruto precisa ser purificado no final da reação para remover o catalisador, glicerol, sabão, óleo e álcool restantes, que podem prejudicar o desempenho do motor. Esse processo gera grandes quantidades de águas residuais que precisam ser descartadas de forma adequada para evitar a poluição do meio ambiente. Este artigo apresenta uma revisão do processo de produção de *biodiesel* e a necessidade de uma etapa de purificação, com foco na geração de efluentes. Métodos tradicionais e avançados para o tratamento de águas residuais provenientes da produção de *biodiesel* são descritos e discutidos. Detalhes sobre patentes publicadas nos últimos cinco anos, relacionadas a técnicas de tratamento dessas águas residuais, também estão incluídos.

Palavras-chave: tratamentos avançados; *biodiesel*; tratamento convencional; poluição; purificação; águas residuais.

INTRODUCTION

The growing demand for energy associated with depleting fossil fuel reserves and the pollution problems arising from the use of this nonrenewable resource, notably the emission of greenhouse gases, are aspects that encourage interest in the use of alternative energy sources, such as biodiesel (MANAF *et al.*, 2019). In all cases, the most commonly used biodiesel production process is transesterification with the use of a homogeneous basic catalyst (e.g., sodium and potassium hydroxides), as this allows a high conversion of fatty acid esters (biodiesel) to be achieved in a relatively short period (CARDOSO *et al.*, 2019).

Although this method is the most widely applied, the use of homogeneous alkaline catalysis has the limitation that it cannot be used for raw materials with high water and free fatty acid (FFA) contents, which may lead to the generation of soaps, therefore reducing the ester yields (GÜNAY *et al.*, 2019). Moreover, it is important to highlight that soap formation makes it difficult to separate the

biodiesel and glycerol phases, leading to the use of greater quantities of water for washing during this purification process.

At the end of the transesterification, the co-product (glycerol) is separated. The crude biodiesel is then purified to remove impurities such as residual glycerol, soap, alcohol, catalyst residue, and FFA which may remain at the end of the transesterification reaction. The purification process is necessary to ensure the quality of the biodiesel produced (FONSECA *et al.*, 2019). There are several methodologies that can be employed to remove impurities; however, wet scrubbing is the most widespread purification process used at biodiesel production plants (ATADASHI, 2015).

Although washing with water is efficient and widely applied after processes where basic or acid homogeneous catalysts are used (ATADASHI *et al.*, 2011; MARCHETTI, 2012), it is associated with problems such as increased time and production cost and difficulty in separating the biodiesel from the water (MANAF *et al.*, 2019). In addition, high water and energy consumption can result (ATADASHI *et al.*, 2011).

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The effluent generated from this process has a high organic load, which increases the values for chemical oxygen demand (COD) and biological oxygen demand (BOD). In addition, there is the presence of oil and grease (O&G) and variations in the pH values, depending on the method used in the production step (COSTA *et al.*, 2017; BASHIR *et al.*, 2018). These aspects mean that treatment is necessary to allow proper disposal. Several methods are available to treat wastewater generated in biodiesel production, including coagulation/flocculation (DAUD *et al.*, 2015), biological treatment (BOONSAWANG *et al.*, 2015), advanced oxidation processes (OPs) (BRITO *et al.*, 2019), or the combination of more than one of these methods (GONÇALVES *et al.*, 2017).

In this context, the aim of this study was to address the main aspects of biodiesel production, focusing on the conflicting issues associated with wastewater generation from the purification step. Also, the traditional and current methods that have been reported in the literature over the past 5 years are described, together with the main patents related to the specific aspects considered.

METHODOLOGY

The methodology adopted to carry out the bibliographic survey, consisted of searching databases, such as Science Direct, Capes Periodicals, Google Scholar, and Google Patents. The keywords used were “biodiesel production,” “purification of biodiesel,” “biodiesel wastewater,” “wastewater treatment,” and “patents.” The articles were selected based on their relevance for the review, with a focus on the generation and treatment of wastewater from the biodiesel production. Research related to coagulation/flocculation and advanced OPs was prioritized, although other treatment technologies were considered for inclusion. Based on this methodology, the inclusion criteria adopted were articles within the topic under study, relevant publications, and prioritizing publications from the past 5 years.

Biodiesel production

Biodiesel production is an attractive way to obtain fuel from renewable sources and the diversity of raw materials that can be used reduces the production costs and energy dependency. Methanol is commonly used as it has low cost and good reactivity. However, the use of ethanol has been reported by some researchers, due to its renewable source and lower toxicity (SINGH; GAURAV, 2018). The transesterification reaction is commonly performed at industrial plants for biodiesel production, and in this reaction, 3 moles of alcohol are required for each 1 mole of triglyceride, thus producing 3 moles of fatty acid esters and 1 mole of glycerol. A catalyst is employed to increase the solubility of the reaction mixture and to accelerate the reaction (SINGH; GAURAV, 2018). The catalysts used can be divided into two groups, namely, homogeneous and heterogeneous, and these can be either acidic or basic (GIRISH, 2018; SUTHAR *et al.*, 2019). The homogeneous catalysts are those that are inserted in the same phase as the reactant in the reaction, whereas the heterogeneous catalysts are present in different physical states either as a solid, liquid, or gas (SINGH; GAURAV, 2018; MIRUS *et al.*, 2019).

The type of catalyst selected is related to the FFA content present in the oil, and, for raw materials with high amounts of these compounds, an acid catalyst is recommended (HELWANI *et al.*, 2009). Basic catalysts are suitable for oils with a low FFA content, as the presence of these compounds can lead to the

formation of a soap and decrease the production of esters (SINGH; GAURAV, 2018). However, in basic homogeneous catalysis, the formation of an emulsion makes it difficult to separate the biodiesel, making it necessary to use more water for the purification, thus generating a high amount of wastewater in the process (ABBASZAADEH *et al.*, 2012).

Due to the inputs required for biodiesel production, the mixture obtained at the end of the reaction contains not only esters but also some impurities, such as FFAs, glycerol, alcohol, catalyst residue, soap, and water (SIDOHOUNDE *et al.*, 2018). These factors influence the quality of the biodiesel and the fuel properties may also be affected due to the presence of polyunsaturated esters, which influences the oxidation or saturated stability and thus the cold flow properties (AMBAT *et al.*, 2018).

Biodiesel purification

The performance of biodiesel is directly dependent on its quality, which is determined by the purification stage, where impurities such as FFAs, glycerol, soap, and catalyst residues are removed (FONSECA *et al.*, 2019). Inefficiently conducting this step can lead to poor engine performance, corrosion, low oxidation stability (ANUAR; ZUHAIRI, 2016), filter clogging, wear, and high carbon deposits (BATENI *et al.*, 2019).

The final biodiesel must meet quality standards, in accordance with the current regulations of each country. These quality standards (listed in Table 1) include those of the American Society of Testing and Materials (ASTM), Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP), and the European Standards (EN).

To ensure quality standards, the purification step must be performed efficiently to meet the criteria of the standards. The purification step can be conducted in two ways: wet wash and dry wash (ATADASHI *et al.*, 2011). Purification using a membrane and pressurized CO₂ has also been reported in the literature (ESCORSIM *et al.*, 2015).

Dry cleaning is performed using ion exchange resins and adsorbent materials, and adsorbents have been specially developed for this purpose, for instance, Amberlite and Magnesol® (ATADASHI, 2015). In recent years, adsorbents obtained from agroindustrial waste have been investigated in order to lower the cost and make the process environmentally friendly. Notable agroindustrial residues that have been studied for this purpose are eggshell (GOMES; PASQUINI, 2018), sugarcane bagasse (FONSECA *et al.*, 2018), and rice husk (MANIQUE *et al.*, 2012). Dry cleaning enables the production of a higher quality of biodiesel in a shorter operating time (ATADASHI *et al.*, 2011; GOMES *et al.*, 2015). Despite the inherent advantages, it is still necessary to

Table 1 – ANP, ASTM, and EN specifications for biodiesel standard.

Properties	Unity	ANP N° 45/2014	ASTM D6751	EN 14214
Ester content, min	% wt	96.50	-	96.50
Acidity index, max	mg KOH g ⁻¹	0.50	0.50	0.50
Free glycerol, max	% wt	0.02	0.02	0.02
Total glycerol, max	% wt	0.25	0.24	0.25
Na + K content, max	mg kg ⁻¹	5.0	5.0	5.0
Methanol or ethanol, max	% wt	0.20	0.20	0.20

Adapted from MAPA (2015).

investigate the disposal of the adsorbents, especially in large-scale processes (KUČEK *et al.*, 2007).

Although the dry cleaning method for biodiesel purification has advantages, hot water wet scrubbing is usually applied at the industrial plants. The process consists of adding a fixed amount of water with gentle agitation to prevent the formation of an emulsion (ATADASHI, 2015). The method is considered to be an effective way to purify crude biodiesel, as it has higher efficiency in removing all of the free glycerol and the impurities from the esters compared to other purification methods. However, it has disadvantages such as a long purification time and the formation of an emulsion, especially when the reaction substrate is waste or has high contents of water, oils, and FFAs (FONSECA *et al.*, 2019; GÜNAY *et al.*, 2019). Table 2 details the advantages and disadvantages of the purification processes employing wet washing and dry washing.

For wet washing, 12–24 h of purification is required compared to just 1–5 h using dry cleaning (ŽIVKOVIĆ; VELJKOVIĆ, 2018). Besides that, as can be seen from Table 2, wet washing produces a large amount of effluent, according to the study by Jaruwat *et al.* (2010), in Thailand, more than 350,000 L day⁻¹ of biodiesel is produced, resulting in the generation of approximately 70,000 L day⁻¹ of wastewater. The washing process is repeated until the water becomes colorless and complete removal of impurities occurs. The pH value of wastewater after treatment must respect the standards in force in each country so that it can be reused or discharged into water bodies. As for example, in Asian countries, the pH range varies between 5 and 9 (DAUD *et al.*, 2015). For proper treatment, it is recommended that the washing process is carried out at least five times and the amount of water used is about twice the amount of biodiesel obtained (OSARUMWENSE *et al.*, 2018). Thus, it is estimated that, in total, for each liter of purified biodiesel produced, a minimum of 10 L of polluted wastewater needs to be treated in accordance with local regulations (SALEH *et al.*, 2010). Figure 1 shows the stages of biodiesel production through transesterification up to the wastewater generation.

Biodiesel wastewater characteristics

Wastewater from the biodiesel purification process (BW) generally has an alkaline pH, high levels of residual oil, BOD, COD, soluble salts (e.g., chloride and sulfate), remained catalyst and residual O&G, and organic substances (e.g., FFAs, methyl esters, acylglycerols, methanol, and glycerol) (VELJKOVIĆ *et al.*, 2014; BRITO *et al.*, 2019), presenting viscosity, and an opaque white color (JARUWAT *et al.*, 2010; GONÇALVES *et al.*, 2017). The amount of wastewater generated in the purification process is 0.2–3 L for each liter of biodiesel

Table 2 - Advantages and disadvantages of wet washing and dry washing on purification crude biodiesel.

Process	Advantages	Disadvantages
Wet washing	Simple and effective; allows use of aqueous acid solutions and biodiesel to meet standard	Longer time; large amount of effluent and reduction of biodiesel yield (formation of free fatty acids and emulsion)
Dry washing	Low-cost natural adsorbents; less time compared to wet washing and allows continuous operation	Requires separate mixing and filtering unit and high cost of commercial adsorbents

Adapted from Suthar *et al.* (2019).

produced, in which this variation will depend on the biodiesel production process (TANATTI *et al.*, 2018; MYBURGH *et al.*, 2019). The inappropriate disposal of this residual water can cause clogging of drains due to the high oil content and can also disrupt biological activity in the sewage treatment process (DAUD *et al.*, 2015; YAU *et al.*, 2018). Some studies have reported the characteristics of wastewater generated in the biodiesel washing process, as shown comparatively in Table 3.

As shown in Table 3, the characteristics of the wastewater vary considerably, which is directly associated with the type of process performed up to its generation. In the study reported by Brito *et al.* (2019), the wash water was obtained from the alkaline transesterification of soybean oil. The crude biodiesel was washed three times with water diluted with a phosphoric acid solution, which resulted in an effluent with a low pH compared to the other wastewater in the table.

Inadequate discharge of this effluent with a high organic load and toxicity is not only associated with sewage clogging but also has a significant environmental impact on water bodies. It can impede the passage of light and hinder oxygen exchange and photosynthesis, besides being associated with eutrophication. In addition, the toxic components of the effluent can be absorbed by the wall/cell membrane of microorganisms and affect their metabolic functions (SILES *et al.*, 2011; JIMÉNEZ-ZAPATA *et al.*, 2017).

Several authors have evaluated the impact of the improper disposal of diluted biodiesel. Leite *et al.* (2011) performed toxicity tests on sea urchins and microalgae in the presence of biodiesel diluted in seawater (1:9, v/v) and observed that methanol was the main toxic contaminant for these organisms. Similar results were reported by Cruz *et al.* (2012), who found that diluted castor oil and cooking biodiesel are toxic to fish, and the main contaminant was also found to be methanol. Müller *et al.* (2019) evaluated the effect of diluted biodiesel on the freshwater microcrustacean (*Daphnia magna*) and marine bacterium (*Aliivibrio fischeri*) and found low toxicity toward the microcrustacean, but for the bacterial species, the biodiesel showed significant toxicity. The presence of methanol

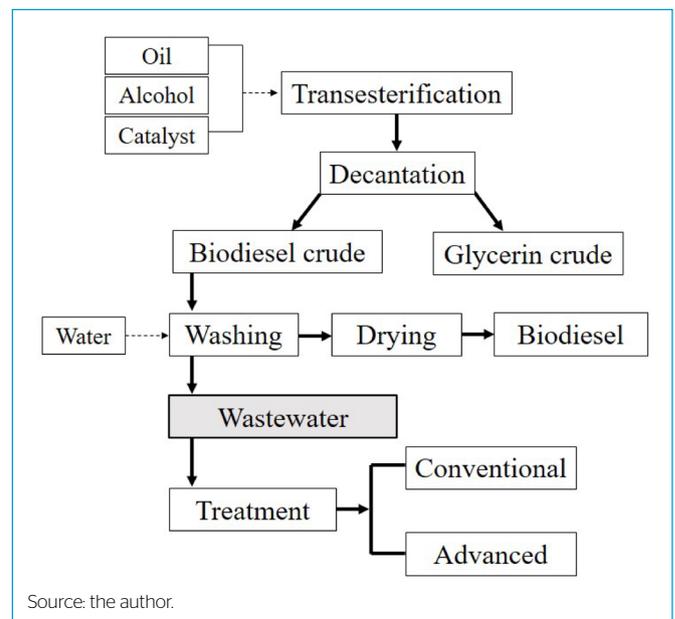


Figure 1 - Biodiesel production stages up to wastewater generation.

Table 3 - Comparison of biodiesel wastewater composition according to the literature.

Source	pH	COD	O&G	TSS	Reference
Previously treated wash water	7.29	3,051	-	3,820	Sassi <i>et al.</i> (2017)
Pretreated by a step of acidification using H ₂ SO ₄	2.90	5,960	1,440	1,000	Costa <i>et al.</i> (2017)
Treated by coagulation-flocculation followed by filtration	9.70	17,016	2,095	3,440	Gonçalves <i>et al.</i> (2017a)
Alkaline transesterification (lab-scale)	9.70	26,376	2,166	5,004	Gonçalves <i>et al.</i> (2017b)
Alkaline transesterification (lab-scale)	2.90	9,935	1,012	-	Costa <i>et al.</i> (2018)
Alkaline transesterification (lab-scale)	6.50	4,550		1,001	Bashir <i>et al.</i> (2018)
Alkaline transesterification (lab-scale)	7.30	5,556	730	-	Stroparo <i>et al.</i> (2018)
Fuel plant	8.30	-	650	3,126	Torres <i>et al.</i> (2018)
Fuel plant	3.85-6.56	88,005	-	-	Daud <i>et al.</i> (2018)
Alkaline transesterification (lab-scale)	1.66	24,210	2,237	-	Brito <i>et al.</i> (2019)

COD: chemical oxygen demand (mg O₂ L⁻¹); O&G: oils and greases (mg L⁻¹); TSS: total soluble solids (mg L⁻¹).

in wastewater is responsible for the rise in the BOD level (VELJKOVIÉ *et al.*, 2014). In many cases, methanol is evaporated; however, traces may remain in the wastewater (BALAT; BALAT, 2010).

No reports were found in the literature for the evaluation of BW in the aquatic environment. However, the studies using diluted biodiesel mentioned above provide an indication of the adverse effects that the improper disposal of this effluent may have on the environment. Further research is, therefore, required to reduce both the generation of BW and its environmental impact. And with a view to reducing the generation of BW, it is necessary to consider all stages of the production process and waste generated. And among the various technologies available for the treatment of wastewater, with conventional and advanced treatments, it is advisable to use economically accessible and environmentally friendly treatments.

The treatments applied can only be used to dispose of wastewater in accordance with regulations, but it can also allow its recovery, for possible reuse. From an economic point of view, any accessible technology can be applied and must guarantee the protection of the environmental quality, conservation of resources, and allow the reuse of water, which will depend mainly on the necessary final quality established by the legislation, according to the country in question (SALGOT; FOLCH, 2018). Among the applications for water reuse, it can be mentioned, use in bathrooms in cases that do not involve direct contact, street washing, sidewalks, dilution of effluents, preparation of steam boilers, heat transfer in heating systems, and liquid soda, among others (GALKINA; VASYUTINA, 2018).

Conventional treatment of BW

Methods that are conventionally applied for the treatment of oily wastewater involve gravity separation and decantation, air flotation, coagulation, demulsification, and flocculation (PUTATUNDA *et al.*, 2019). According to the study by Veljković *et al.* (2014), flocculation or sedimentation steps, biological treatment, and reverse osmosis systems have also been employed for wastewater treatment.

Regarding the biological treatment system, anaerobic digestion is often employed, as reported by Queiroz *et al.* (2016), in which the authors used the anaerobic treatment of the biodiesel effluent, verifying the removal of 60% of COD and significant energy recovery in the form of methane gas. However, this treatment is not always feasible, since the wastewater from

biodiesel production has a high content of long chain fatty acids, which have acute toxicity toward the anaerobic consortium, harming cell transport, or cell protection functions of the microorganisms (RINZEMA *et al.*, 1994). In addition, the presence of high amounts of solids in the BW inhibits the growth of microorganisms and decreases the removal efficiency of the biological treatment (DAUD *et al.*, 2015). Another factor that hinders the use of this treatment is the acute toxicity of the BW, detected through testing, using *Vibro fischeri* bacterium possibly due to the presence of fats, alcohol, and the catalyst (JIMÉNEZ-ZAPATA *et al.*, 2017).

Coagulation/flocculation is widely applied because of its simplicity and cost-effectiveness. It can be employed in conjunction with other techniques such as a pre-treatment or post-treatment procedure, depending on the characteristics of the water to be treated (TZOUPANOS; ZOUBOULIS, 2011). In these processes, a previous step with pH adjustment is usually required, and the commonly applied coagulants are aluminum sulfate (TORRES *et al.*, 2018) and ferric chloride (GONÇALVES *et al.*, 2017). Despite being widely used, it has the disadvantage of using chemical products that lead to the formation of a large volume of sludge, which makes its disposal more expensive. Furthermore, due to its toxicity, its reuse is impracticable (TEH *et al.*, 2016).

Some studies have produced important results regarding the application of the coagulation/flocculation process in the treatment of wastewater from biodiesel production. Torres *et al.* (2018) applied this treatment procedure to raw effluent and achieved a reduction of ~60% in the total organic carbon (TOC) content, demonstrating the need to implement additional treatment, since the percentage of remaining TOC was high. While Daud *et al.* (2018) reported the removal of turbidity, COD, and soluble solids (32%, 34%, and 39%, respectively). Stroparo *et al.* (2018) evaluated the use of chitosan as an alternative to the conventional chemicals and reported removals of 94% and 70% of COD and O&G, respectively; although the reduction in pollutant compounds presented by the authors was high, the wide range of contaminants present in the BW must be considered.

In the case of a study by Gonçalves *et al.* (2017b), reductions of ~82% for O&G and ~35% for COD were obtained, with similar results for both aluminum (Al³⁺) and ferric ion (Fe³⁺) coagulants, noting that there was low COD removal with a value close to that reported by Daud *et al.* (2018); in addition, only 34% of the toxicity was removed, emphasizing the need for additional treatment.

On applying this procedure as a pretreatment, Gonçalves *et al.* (2017a) used Al^{3+} and achieved a 98% reduction in turbidity, apparent color, soluble solids, and O&G. Costa *et al.* (2018) also used this process as a pretreatment and reported reductions of 10% for COD and 78% for O&G; however, the organic load of the effluent remained high and the authors considered implementing an additional step later.

The application of the abovementioned processes is often not sufficient to obtain an effluent that meets the parameters required by the environmental inspection units. Thus, further studies focused on advanced treatments that increase the removal of pollutants present in the wastewater are required. In addition, in this regard, the purification process needs to be improved as wastewater generation continues to increase and reports on studies addressing this issue are scarce (DAUD *et al.*, 2015; ŽIVKOVIĆ; VELJKOVIĆ, 2018).

Recent trends in BW treatment

The advanced processes are of great interest in the treatment of effluents with high organic load or with toxic characteristics (COSTA *et al.*, 2017), issues often associated with wastewater resulting from biodiesel washing (BRITO *et al.*, 2019). These processes are often applied in combination, together with a pretreatment step involving flocculation/coagulation.

The advanced technologies that have been applied in recent years for the treatment of wastewater generated during the purification of biodiesel include OPs and advanced oxidation processes (AOPs). In OPs, there is the direct

addition of oxidants, such as H_2O_2 , $NaClO$, and $KMnO_4$ (WEI *et al.*, 2019), and AOPs can involve different methods, including the Fenton reaction, where the hydroxyl radical acts as an oxidant of organic species, which can be performed through the catalytic decomposition of hydrogen peroxide in the presence of an aqueous solution of iron ions (Fe^{2+}) (Bagal and Gogate, 2014). In the photo-Fenton process, the oxidation occurs under UV irradiation in the presence of ferric ion in acid medium, causing the formation of hydroxyl radicals (NOGUEIRA *et al.*, 2007).

In this context, in addition to the abovementioned technology, other treatments can be used. Table 4 presents data from the literature regarding the ability to remove TOC, BOD, COD, and O&G, as well as the characteristics of BW before the treatment. As shown in the table, different types of treatments also result in variation in the ability to remove TOC, BOD, COD, and O&G. Electrooxidation and electrocoagulation are called electrochemical treatments, and these treatments are known for their high efficiency, low need for treatment space, and ease of operation (GUO *et al.*, 2017). Electrooxidation showed efficiency in reducing COD and O&G of BW (JARUWAT *et al.*, 2016), and electrocoagulation resulted in high removal of DOC and TOC (TANATTI *et al.*, 2018). In addition, the combination of treatments, flocculation/coagulation and electrochemical, has also been shown to be effective, in terms of the removal of organic load and toxicity of BW (TORRES *et al.*, 2018).

The combination of treatments is relevant for complex effluents, such as biodiesel, and allows combining the efficiency of physical/chemical/

Table 4 – Comparison of the use of different technologies in the treatment of biodiesel wastewater.

Treatment	Wastewater characteristics*	% Removal				Reference
		TOC	BOD	COD	O&G	
Electrooxidation (Ti/RuO ₂)	BOD 168,000-300,000 COD 321,000-855,000 O&G 18,000-22,000	nr	41	63	97	Jaruwat <i>et al.</i> (2016)
H ₂ O ₂ /UVC	COD 5,960 BOD ₅ 2,890 O&G 1,440	nr	76 ²	78	nr	Costa <i>et al.</i> (2017)
FM ¹ and Fenton	COD 17,016 O&G 2,095	nr	nr	90	98	Gonçalves <i>et al.</i> (2017a)
Oxidation and Coagulation	COD 2,954	nr	nr	82	nr	Yang <i>et al.</i> (2017)
Wet air oxidation	COD 4,310 TOC 1,050	45	nr	55	nr	Solís, Rivas and Sol. (2019)
Electrocoagulation	TOC 98,120 COD 399,800 O&G 25,000	92	nr	92	nr	Tanatti, Sengil and Ozdemir (2018)
Flocculation/coagulation and electrochemical	TOC 6,004	78	nr	nr	nr	Torres <i>et al.</i> (2018)
Flocculation/coagulation and photo-Fenton	COD 9,935 BOD ₅ 5,390 O&G 1,012	nr	88 ²	72	78	Costa <i>et al.</i> (2018)
HMBB ³	TOC 1,257 COD 4,061 BOD 1,649 O&G 1,232	68	nr	69	nr	Gonçalves <i>et al.</i> (2019)
Fenton	TOC 1,257 COD 4,061 BOD 1,649 O&G 1,232	nr	nr	90	nr	Gonçalves <i>et al.</i> (2019)

nr: no reported.

biological processes, which is interesting, especially in the case of recalcitrant compounds, which are hardly removed by conventional methods (BHANOT *et al.*, 2020). In this context, combined treatments have aroused the interest of researchers to evaluate the combination of two or more treatments; as an example of combined treatments, we have radiation UVC and H₂O₂ (COSTA *et al.*, 2017), oxidation and coagulation (YANG *et al.*, 2017), membrane filtration and Fenton (GONÇALVES *et al.*, 2017), flocculation/coagulation and electrochemical (TORRES *et al.*, 2018), and HMBB/Fenton (GONÇALVES *et al.*, 2019), and among these, FM-Fenton resulted in greater removal of COD and O&G.

Solis *et al.* (2019) reported that BW had low biodegradability (BOD/COD ratio = 8.6×10^{-3}), making the application of wet air oxidation (WAO) treatment conducive, in which the insoluble organic matter is transformed into simpler soluble compounds. WAO occurs through a radical oxidation mechanism involving organic radicals and peroxides; however, a recalcitrant effect was noted, probably due to the high temperature resistance of the oxidation intermediates generated after treatment. And as mentioned earlier, Gonçalves *et al.* (2019) performed the combined treatment of HMBB/Fenton. Such treatment was proposed using only HMBB, as the BW was not yet suitable for disposal. The application of the combined treatment resulted in high removal of COD, turbidity, and O&G, eliminating the acute toxicity.

It is noteworthy that most of the treatments resulted in relevant data regarding the reduction of potentially polluting compounds; however, some authors did not evaluate the toxicity of BW before and after treatment (JARUWAT *et al.*, 2016; YANG *et al.*, 2017; FERNANDES *et al.*, 2018; TANATTI *et al.*, 2018). For treatments that employ photo-Fenton or Fenton, consider the analysis of fundamental toxicity, since residual H₂O₂ can have a toxic effect (GONÇALVES *et al.*, 2017; PÉREZ-MOYA *et al.*, 2017), not contributing to the reduction of dangerousness in the BW even after treatment. It is important to mention that the decrease in toxicity can minimize the environmental impact caused by the BW and can enable the reuse of the effluent after treatment. Besides that, studies involving a complete economic analysis of the treatments as well as cost-benefit analysis are still scarce in the literature.

Overview of patents related to BW purification

In view of what was discussed in the previous items, the need for further studies and investments on efficient technologies for the treatment of BW becomes evident. In this sense, Table 5 provides information about patents

Table 5 - Published patents on biodiesel wastewater treatment.

Patent	Treatment type	Reference
CN105984999	Conventional	Bingna <i>et al.</i> (2016)
CN106365380	Conventional	Xin <i>et al.</i> (2016)
BR 1020150309759	Combined ¹	Soletti <i>et al.</i> (2017)
CN106830504	Conventional	Zhenhong <i>et al.</i> (2017)
WO/2018/221759	Conventional	Lee <i>et al.</i> (2018)
KR20180131669A	Conventional	Lee <i>et al.</i> (2018)
CN109052832A	Combined ¹	Leping <i>et al.</i> (2018)
CN208008650U	Conventional	Zhao <i>et al.</i> (2018)

¹Application of two or more methods (conventional and advanced method).

filed in the past 5 years, related to the treatment of residual water from biodiesel production.

It is clear from the technologies detailed in Table 5 that the focus is still on conventional treatments, highlighting anaerobic and aerobic treatments (BINGNA *et al.*, 2016; LEE *et al.*, 2018a, 2018b). In addition, the inclusion of a treatment step with activated charcoal was also reported (ZHAO *et al.*, 2018). These treatments proved to be efficient in terms of their ability to remove organic pollutants. A proposal different from the others was described by Zhenhong *et al.* (2017), in which the treatment process includes the steps of anaerobic fermentation and purification with aquatic plants (*Eichhornia crassipes*). According to the researchers, after these processes, the wastewater reaches the standard for disposal.

The combined approaches reported involved the use of recent treatments. The patent filed by Soletti *et al.* (2017) describes the use of electrochemical techniques, followed by Fenton's reaction and chemical coagulation to remove organic matter present in BW. According to Leping *et al.* (2018), the proposed system (advanced treatment) is suitable for the treatment of wastewater with a high COD content. The authors present a wastewater classification according to the concentration of pollutants that can be easily degraded. They propose that with the application of advanced oxidation treatment, macromolecular organic pollutants that are difficult to degrade in sewage are converted into small, easily degradable molecular substances.

CONCLUSION

The implications of the high amounts of wastewater generated during biodiesel production, which needs treatment, were addressed in this study, and the conventional and advanced treatment technologies available were discussed. Important issues must be considered, not only the production of biofuels but also the resources that are used for production, such as energy and water, in addition to the waste that will be generated at the end of the process, whether solid or liquid. In general, the treatment used in these generated effluents will depend on the technology available in the locality and the financial capacity of the industry in question. However, the inadequate or inefficient treatment of the waste water generated can have an impact on the environment; in this sense, the laws and regulations that define the final quality of treated water must be obeyed. Conventional methods are often not sufficient to eliminate the toxicity of the effluent. Advanced and combined treatments employing the photo/Fenton reaction demonstrate results that set them apart in terms of efficient wastewater treatment. However, further research is needed to analyze the pollutant removal efficiency associated with the process cost. Based on the discussion presented, expect that the inputs and industrial processes for the production of biodiesel will be improved in order to reduce the volume of waste generated. Further research is still needed in order to make the use of efficient technologies for the treatment of waste water viable, which may also enable the creation of a unified regulation for the final quality of treated waters to be discarded or reused.

AUTHORS' CONTRIBUTIONS

Postaue, N.: Writing – original draft, review & editing. Fonseca, J. M.: Writing – review & editing. Bergamasco, R.: Conceptualization. Da Silva, C.: Conceptualization, Project administration, Supervision.

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