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A Comparison between Coagulation and Ultrafiltration Processes for Biodiesel Wastewater Treatment

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The progressive increasing on biodiesel production has been generating a large amount of wastewater due to the biodiesel purification process. The present work aims to develop and evaluate different processes to improve the quality of biodiesel wastewater to achieve legislation requirements for its final disposal. In order to do that membrane filtration and coagulation processes were tested. Micro and ultrafiltration ceramic membranes obtained by isostatic pressing were used for the cross-flow filtration process and tannin coagulant (Tanfloc SG) was employed in the coagulation process. A pre-treatment for grease removal was accomplished by adding sulfuric acid the wastewater until pH 2.5.
Ultrafiltration membrane (alumina-zirconia and sintered at 1,500 °C) showed better results for color, turbidity and Chemical Oxygen Demand (COD) removal. These tests were conducted at a transmembrane pressure of 2 bar and keeping constant the other operational parameters. Once the best membrane was determined, the variation of transmembrane pressure was investigated by increasing it to 3 bar. The alumina zirconia ultrafiltration membrane, using the pre-treated wastewater, had a COD, color and turbidity removal of 19.5, 74.1 and 100%, respectively. The biodiesel wastewater was submitted to coagulation experiments for different pH values and tannin concentration. Through the coagulation tests, the pre-treated effluent with the higher tannin concentration, at pH of 8, had better results when compared to the untreated wastewater.
The best coagulation results showed a COD, color and turbidity removal of 73, 69 and 75%, respectively. Both ultrafiltration and coagulation presented good efficiency for organic matter removal, but the coagulation process reached higher COD removal.

1. Introduction

The progressive increasing on petroleum price, as well as the environmental impact caused by gas emissions, is one challenge that the society is facing nowadays. As a result, in order to supply the global energy demand, biomass has been an alternative for diversifying energy sources. Biomass is pointed as a viable and sustainable fuel resource, once it is economic and environment-friendly. Within this energy scenario, biodiesel appears as an alternative to fossil fuels, extremely favorable, including in the social and economic aspect. Thus, biodiesel has been gaining ground in the domestic and global markets, increasing its production level each year. This increasing in biodiesel production is followed by an increasing in wastewater generation. The major amount effluent is generated during the biodiesel purification process, which is done to achieve market's specifications. In this context, studies have been emerging for developing new wastewater treatment processes under the environmental legislation requirements (IAP, 2011).
As the transesterification reaction proceeds, biodiesel separates from glycerol by decantation. Then, the biodiesel is submitted to a purification process, followed by filtration and drying operations. The purification step consists on biodiesel water-washing for impurities removal. The wastewater generated by washing consists, basically, on soap, fatty acid, alcohol, glycerol and others minor contaminant. The production of 100 L of biodiesel generates, depending on the impurity degree, from 20 to 300 L of wastewater. This wastewater

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has to be treated in order to be dumped on water bodies or recovered for reuse. Moreover, the treatment in which the effluent is submitted has to achieve the legislation requirements.

Among all treatment processes, there are the flocculation/coagulation/flotation, eletrochemical, biological and filtration treatments (Daud et al., 2015; Veljković et al., 2014). The coagulation with chemical coagulant, such as ferrous sulfate ($FeSO_4$), ferric chloride ($FeCl_3$) and aluminum sulphate ($Al_2(SO_4)_3$), is commonly used. Kumjadpai et al. (2011) investigated the biodiesel wastewater treatment by pretreating it with H_2SO_4 until pH 1-2.5 and then, adding $Al_2(SO_4)_3$, a chemical coagulant. By doing that, a removal of 98.3% COD, 97.7% BOD_5 and 99.2% of fatty acid was obtained. Veljković et al. (2014) studied various biodiesel wastewater treatment processes. After the data analysis, it was concluded that proper acidification and chemical coagulation/flocculation successfully remove grease and oil but they are unsuccessful for removing COD. Some inorganic coagulants are equally effective for the removal of residual oil and COD. In addition, coupled acidification and chemical coagulation is efficient in removing both pollutants. The electrochemical treatment is characterized by the same efficiency as the chemical one. The combinations of chemical methods (acidification, coagulation) with the electrochemical treatment improve the removal efficiencies of COD and BOD, compared to both individual treatment processes.

Most of papers cited in the literature have been using inorganic coagulants for treating biodiesel wastewater. These coagulants are not expensive; however they generate a non-environmental friendly sludge. Organic or natural coagulants can be used instead of the inorganic ones, once they produce a biodegradable sludge, which has low toxicity. Among the organic compounds with coagulant, flocculant and adsorbent properties, the most efficient are chitosan, *Moringa oleifera* Lam., and tannins. Tanfloc SG is a tannin − a low molecular weight cationic organic polymer, biodegradable and basically constituted by quaternary ammonium tannate. Aiming at investigating the potential of this natural coagulant to improve quality of biodiesel wastewater, its efficiencies and applicability will be evaluated on this paper.

Among the wastewater treatment methods mentioned, membrane filtration has not been much investigated as a method of treatment for the effluent under study. Hashlamon et al. (2017) related the use of nanofiltration for diluted biodiesel wastewater treatment which was pretreated using a combination of powdered-activated carbon (PAC) adsorption and membranes CFS (PAC/CFS). Other authors has been applied the method of membrane filtration to the purification of biodiesel and glycerin itself (Gomes, 2013; Atadashi et al., 2011) and some others in the treatment of different types of industrial wastewater (Stoller et al., 2016; Almandoz et al., 2015) by using commercial ceramic and / or polymer membranes. In the present paper micro and ultrafiltration ceramic membranes produced by differentiated method (isostatic pressing) were evaluated for biodiesel wastewater treatment and then, a comparison of this technique with coagulation process was performed aiming achieving high efficiency with respect to the removal of organic matter.

2. Materials and methods

In order to develop this investigation, tubular ceramic membranes made by isostatic pressing (Del Colle, 2011) were used for the cross-flow micro and ultrafiltration experiments. For the coagulation study, tannin (Tanfloc SG) was applied as a natural organic coagulant. Moreover, the industrial wastewater used was from biodiesel purification process in which the raw material used is a blend of soybean oil and bovine tallow. The experimental analysis was focused on the separation process efficiency, in a way to compare the membrane filtration and the coagulation operations.

2.1 Biodiesel wastewater pre-treatment

Before the coagulation and filtration experiments, a pre-treatment was conducted on the biodiesel wastewater for fatty matter removal. The pre-treatment was carried out by addition of concentrated sulfuric acid (Synth), under constant stirring and room temperature, up to the pH be on the range 1.5-2.0. After that, the acidified sample of wastewater was placed in a separating funnel for phases separation. The less dense phase containing fatty matter was discarded.

2.2 Biodiesel wastewater treatment by coagulation

Preliminary tests were performed in order to find the best coagulation parameters, such as pH, coagulant concentration and coagulant-effluent weight mass ratio, from pre-treated biodiesel wastewater sample. Coagulation tests using pre-treated biodiesel wastewater sample were conducted with and without pH correction in a range from 5 to 8. The pH was corrected by using a calcium hydroxide (1 M) solution, under constant stirring (magnetic stirring). After the organic coagulant addition, the solution was vigorously stirred for 5 minutes, followed by 20 minutes of slowly agitation (with magnetic stirrer − FISATOM). After, the solution rested for 12 hours until decantation. Once it has decanted, the supernatant was collected for color, turbidity, COD and pH analysis. The analysis pointed the best coagulation parameters, which were reproduced in a *Jar* *test* (MILAN/model-101) at 70 rpm for 5 minutes and 140 rpm for 20 minutes, and then, the supernatant was collected for physic-chemicals analyses (in duplicate) and the sludge was discarded.

2.3 Biodiesel wastewater treatment by cross-flow micro/ultrafiltration

The micro and ultrafiltration test were performed in a NETZSCH pilot membrane filtration unit, model 027.06-1C1/07-0005/AI (Gomes, 2013). The industrial biodiesel wastewater used in this work was collected at BS BIOS mill (Marialva, Brazil) and kept under refrigeration at 3 ºC. Tests were conducted for 60 minutes by using 3 L of wastewater, at 690 L/h flow rate, constant temperature (14 ± 1 °C) and pressure (2 bar). The fluid dynamic performance was analyzed through the permeate flux in relation to the process duration time. The permeate flux (J) was calculated according to Equation (1):

$$J = m_p/(A_p \times t) \quad (1)$$

Where:
m_p: permeate weight mass (Kg) at time t;
A_p : permeation area (m²);
t: time (s).
The best membrane was chosen after doing some preliminary tests using different ceramic membranes: porous alumina membrane with a mean pore size of 0.8 µm; alumina-zirconia membrane (sintered at 1,500 °C): mean pore size of 0.03 µm; alumina-zirconia membrane (sintered at 1,400 °C): mean pore size of 0.1 µm and zirconia-zirconia membrane: mean pore size of 0.01 µm. After the preliminary tests and permeate analysis the permeate quality was evaluated in order to choose the best operating membrane. The better membrane selected used for new a experiments at a transmembrane pressure of 3.0 bar but, keeping the same flow rate, temperature and operating time. Membranes cleaning were performed at the unit after each experimental batch with water and neutral soap and then, it washed with sodium hydroxide (0.1 M) solution. After that, the membranes was placed in a sodium hydroxide (0.1 M) solution, cleaned in an ultrasound bath (THORNTON) for 30 minutes and kept in distillated water for 48 hours.

2.4 Physical-chemical analysis

Raw biodiesel wastewater, pre-treated wastewater effluent, supernatant (after coagulation), permeate and concentrated (after membrane filtration) were analyzed in relation to pH, color, turbidity and COD according to the standard procedures for wastewater analysis – Standard Methods for The Examination of Water and Wastewater (Eaton et al., 2005). Sample's pH were measured through a digital pH-meter (DIGIMED), at room temperature. Color, turbidity and COD analysis were performed at a spectrophotometer (HACH – DR/2010), in duplicate. The efficiency of the treatment, expressed as percentage of removal, for color, turbidity and COD analysis, was calculated according to Equation (2):

$$\%R = (1 - C_a/C_b) \times 100 \quad (2)$$

Noting that:
C_a is the concentration after the treatment and C_b the concentration before the treatment.

3. Results and discussion

3.1 Coagulation tests

In order to determine the better coagulant concentration, preliminary coagulation tests were performed by varying tannin (Tanfloc SG) concentration (50 and 80 g/L) to be used on the pre-treated biodiesel wastewater and with adjusted pH before coagulation. The coagulant solutions were added on the pre-treated wastewater (pH adjusted to 8) at a ratio of 1:2.
As shown in Table 1, the coagulant concentration had a considerable influence on the removal parameters. An increasing on coagulant concentration improved COD, turbidity and color removal in more than 60%. Once the influence of concentration was determined, another batch of experiments using the pre-treated wastewater was performed by varying the adjusted pH value (5 and 7) before coagulant addition. For the new experiments, the coagulant-effluent ration was of 1:2 for tannin concentration of 80 g/L.
For comparison purposes, tests were also performed with raw and pre-treated wastewater without pH adjustment. Results are presented on Table 2.

Table 1: Physical-chemical analysis of raw and pre-treated wastewater (without addition of coagulant solution) and treated wastewater by coagulant solution in different concentrations.

Parameters	Raw wastewater	Pre-treated Wastewater	Treated wastewater – Coagulant concentration (50 g/L)*	Treated wastewater – Coagulant concentration (80 g/L)*
COD[1] (mg/L)	494,750	484,600	279,200	133,500
Color[2] (mg Pt-Co/L)	725	525	487.5	225
Turbidity[3] (FAU)	100	25	25	25
pH	6.15	2.0	7.18	4.81
COD removal (%)	___	2.1	43.6	73
Color removal (%)	___	27.6	32.8	69
Turbidity removal (%)	___	75	75	75

[1]sample diluted in a ratio of 1:1,000 (v/v); [2] sample diluted in a ratio of 1:50 (v/v); [3] sample diluted in a ratio of 1:25 (v/v).

Table 2: Physical-chemical analysis of raw, pre-treated wastewater and of treated wastewater by adjusted pH variation (before coagulation).

Parameters	Raw wastewater	Pre-treated wastewater	Treated wastewater – Coagulation (pH 5)*	Treated wastewater – Coagulation (pH 7)*
COD[1] (mg/L)	241,100	256,150	236,450	204,350
Color[2] (mg Pt-Co/L)	650	4,600	775	1,050
Turbidity[3] (FAU)	50	475	25	25
pH	4.90	2.00	4.25	5.90
COD removal (%)	49	48	52	59
Color removal (%)	10.4	___	___	___
Turbidity removal (%)	50	___	75	75

[1]sample diluted in a ratio of 1:1,000 (v/v); [2] sample diluted in a ratio of 1:50 (v/v); [3] sample diluted in a ratio of 1:25 (v/v).

As noticed on Table 2, an increasing on pH also increases COD and turbidity removal parameters. On the other hand, it is noticiable the increasing in color, in comparison to the raw wastewater. At low pH range, as for pre-treated wastewater (pH around 2), the coagulant activity is unfavorable, leading to low COD removal and an increasing on color and turbidity. Aiming to increase the COD removal parameter, coagulant-effluent ratio was modified from 1:2 to 1:4, keeping the same values for other parameters. As a result, then final COD dropped from 494,750 to 194,300 mg/L. Thus, the best coagulation parameters are: pH 8, coagulant concentration of 80 g/L and coagulant-effluent ratio of 1:2. Even though the mentioned better conditions improved the biodiesel wastewater quality, the organic matter is still high requiring an improvement in the treatment to reach the standard required (COD: 300 mg/L) by state environmental legislation (IAP, 2009).

3.2 Cross-flow micro/ultrafiltration tests

Micro and ultrafiltration ceramic membranes were applied on filtration for biodiesel wastewater treatment. The process efficiency was based mainly on the fluid dynamic behavior and on fatty matter removal. Among all the used membranes (cited on section 2.3), at the same operating conditions, zirconia-zirconia membrane (0.01 μm) had the higher permeate flux for 60 min. operating time. On the other hand, alumina-zirconia membrane (0.03 μm) showed the worst permeate flux behavior, as shown in the figure 1(a).

This difference on the flux behavior is due not only to the difference in membrane structure (pore size, total and apparent porosity, composition), but also due to the selectivity of the membrane material in relation to the components of the mixture or study fluid. Thus, the membrane polarized layer will differ from one to another membrane and promote a great influence on the permeate flux. As the polarized layer increases, the retention coefficient also rises. A resistance against the tangential flux appears and generates a decrease on the permeate flux. That is in accordance to the experiments results.

The alumina-zirconia membrane (0.03 μm) had the worst fluid dynamic behavior, but the greater retention coefficient, which leaded to higher color, turbidity and COD removal. Once the alumina-zirconia membrane had the best retention results, it was used for posterior ultrafiltration tests at different transmembrane pressures (figure 1b).

Figure 1 (b) illustrates that when compared to the process operated at 2 bar, the fluid dynamic behavior improves when operated at 3 bar, as the driven force is increased for the ultrafiltration membrane (alumina-zirconia).

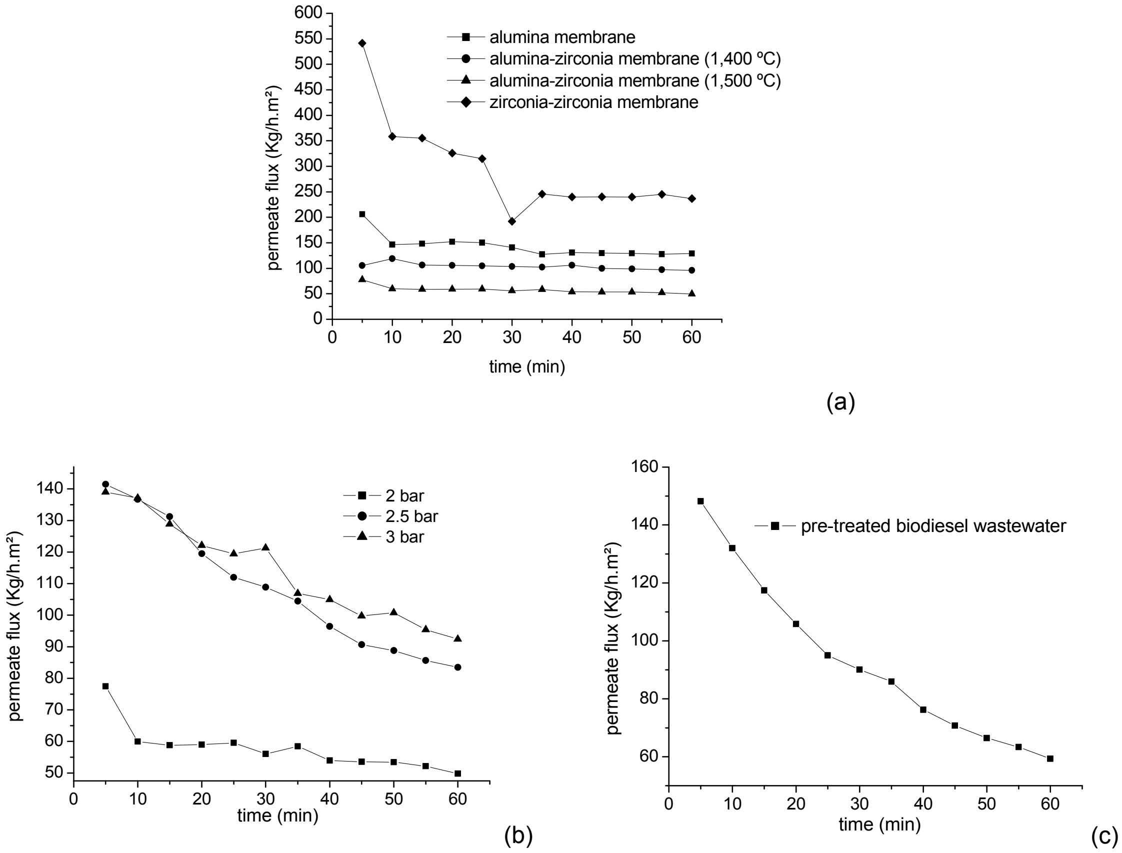

Figure 1: Comparison of fluid dynamic performance for different ceramic membranes (a); influence of the transmembrane pressure (b) and pre-treatment (c) on the permeate flux in relation to the process operating time for the alumina-zirconia membrane.

In order to obtain better fluid dynamic behavior, the pre-treatment with sulfuric acid was applied to the raw wastewater for its fatty matter removal. This pre-treated wastewater was used for a new experiment at 3 bar. Figure 1(c) shows an increase on the fouling for the pre-treated wastewater when compared to the without treatment wastewater at 3 bar. The pre-treatment reduces the pH of the biodiesel wastewater, changing the membrane selectivity and improving the membrane-wastewater interaction. As a result, the polarized layer increases and may cause clogging on the membrane surface and in pores, which limits the fluid permeation. In addition to the fluid dynamic behavior and retention coefficient, physical-chemical analysis were performed for both permeate and concentrate, as shown on Table 3.

Table 3: Physical-chemical analysis of raw wastewater and pre-treated and treated effluent for ultrafiltration.

Parameters	Raw Effluent	Permeate after ultrafiltration	Permeate after pre-treatment and ultrafiltration
COD[1] (mg/L)	494,750	467,750	398,500
Color[2] (mg Pt-Co/L)	725	87.5	187.5
Turbidity[3] (FAU)	100	12.5	0
pH (final)	6.15	6.00	3.05
COD removal (%)	___	5.5	19.5
Color removal (%)	___	87.9	74.1
Turbidity removal (%)	___	87.5	100

[1]sample diluted in a ratio of 1:1,000 (v/v); [2] sample diluted in a ratio of 1:50 (v/v); [3] sample diluted in a ratio of 1:25 (v/v).

Although great color and turbidity removals were achieved in both methods (ultrafiltration without and with pre-treatment), the ultrafiltration membrane was not able to efficiently retain the small molecular weight dissolved chemical species present in the biodiesel wastewater, such as methanol, glycerides, glycerin and other compounds that are loaded during washing and centrifugation - biodiesel purification step. However, the pre-treatment provided an improvement on the COD and turbidity removal, but the wastewater pH decreases and needs to be adjusted (for pH 5) before discard the effluent. It is important to emphasize that fatty and organic matter concentration can vary greatly depending on the raw material used for biodiesel production and the purification method used, influencing COD removal.

4. Conclusions

The biodiesel wastewater treatment by filtration membrane demonstrated that the ultrafiltration membrane (alumina-zirconia and sintered at 1,500 ºC) can give better results in respect to the fluid dynamics behavior and organic matter retention at a transmembrane pressure of 3 bar. After the pre-treatment of the wastewater; the coagulation process performed by an organic coagulant presented better results for the pre-treated wastewater with the biggest tannin concentration and at pH of 8.
The comparative study demonstrated that coagulation was more efficient than ultrafiltration in COD removal; since ultrafiltration was more efficient in removing color and turbidity (it retained better the suspended particles but not most of the dissolved particles). For this case study, both techniques show to be efficient on biodiesel wastewater treatment, but the high organic matter concentration presented in the wastewater did not decreased sufficiently to achieve the legislation requirements for final disposal of the treated wastewater.
This is not to say that these techniques cannot be used for other biodiesel wastewater with lower organic matter concentration than presented on this study. In this regard, they can be considered environmentally friendly.

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