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Ferrer-Polonio, E.; Iborra Clar, A.; Mendoza Roca, JA.; Pastor Alcañiz, L. (2016). Fermentation brines from Spanish style green table olives processing: treatment alternatives previous to recycling or recovery operations. *Journal of Chemical Technology and Biotechnology*. 91(1):131-137. doi:10.1002/jctb.4550.



The final publication is available at

<http://dx.doi.org/10.1002/jctb.4550>

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Fermentation brines from Spanish style green table olives processing: treatment alternatives before recycling or recovery operations

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Abstract

BACKGROUND: Fermentation brine from Spanish style green table olives processing (FTOP) is characterized by very high conductivity (around $88 \text{ mS}\cdot\text{cm}^{-1}$), high values of suspended solids (near $1300 \text{ mg}\cdot\text{L}^{-1}$), chemical oxygen demand (around $17900 \text{ mg}\cdot\text{L}^{-1}$) and total phenols ($1000 \text{ mg}\cdot\text{L}^{-1}$). In this paper, fermentation brines have been exhaustively characterized and pH adjustment-sedimentation, coagulation-flocculation-sedimentation and adsorption with activated carbon have been evaluated.

RESULTS AND CONCLUSIONS: The pre-treatment selection will depend on the final FTOP management. If no polyphenols elimination is required in view of a further recovery, the best pre-treatment is pH adjustment to 9 plus sedimentation. The removal efficiency achieved were 33.1% solid suspended, 82.5% turbidity and only 10.4% of polyphenols. However, if the final FTOP treatment was biological, the best pre-treatment is adsorption with powder active carbon, because this pre-treatment implies the maximum reduction of phenols in FTOP, which inhibit microorganism activity in the biological process. The maximum in total phenols removal efficiency was 96.0% with $8 \text{ g}\cdot\text{L}^{-1}$ of BM8 powder activated carbon (21% soluble COD).

Keywords: Fermentation brines; Polyphenols; Pre-treatments; Table olives.

VI.1.1.1. Introduction

Table olives production is mainly concentrated on Mediterranean countries such as Spain, Italy, Greek, Tunisia and Morocco [1]. In particular, Spain is the biggest table olives producer in the World. The average world production was between 2005 and 2011 of 2,150,000 tonnes, corresponding 508,000 to the Spain's production, i.e. 24% of the world production [2].

The aim of the table olive processing is to convert the olive tree fruit into an edible product by eliminating its bitterness, which is mainly due to oleuropein. This is a polyphenol that can only be found in olives. The process firstly includes the treatment with sodium hydroxide solution (1-2% w/v) during 8-12 hours. In this stage, oleuropein is hydrolysed [3]. Sodium hydroxide penetrates through approximately three quarters of the fruit flesh, remaining a flesh volume around the bone unaffected. This unaffected part will provide the sugar content for the further fermentation. After this stage, olives are rinsed and submerged in brine (4-8 % w/v) of sodium chloride and lactic acid is added for pH adjustment. The organoleptic properties of olives are improved by this solution, enhancing simultaneously the growth of *Lactobacter lactobacillus*, which is responsible for the fermentation. This stage is slow (around 2 months). After it, table olives are prepared for their use.

Wastewater generated during fermentation process of table olives processing (FTOP) is in the range of 3.9 and 7.5 m³ per ton of olives [1]. This volume is only 20% of the total wastewater produced by a table olive processing industry but it contributes to 80-85% of the total pollution [4]. The simultaneous presence of high organic matter and phenolic compounds (soluble COD around 17.9 g·L⁻¹ and total phenols concentration of 1045 mg·L⁻¹) and the enormous conductivity (around 88 mS·cm⁻¹) due to the high salt concentration make difficult the brine treatment. Thus, Romero-Barranco et al. [5] proposed some general guidelines for the treatment of spent brines or osmotic solutions, highlighting the main difficulties in their treatment. These authors proposed the conventional physic-chemical processes (adsorption with activate carbon and ultrafiltration) as pre-treatments, although they no reported results in term of removal efficiencies.

The biological treatment of these effluents is also very difficult to carry out. The salinity shocks by fermentation brines or osmotic solutions discharged to municipal wastewater treatment plants cause physical and biochemical changes of the activated sludge [6]. If a separated biological treatment is carried out for the fermentation brines, the high salinity and the phenols concentration will require very high hydraulic retention times in the reactors. Additionally, the adapted biomass or isolated bacterial strains will be necessary due to the inhibitory effect in the biomass of phenolic compounds and salt concentration [7, 8].

Unlike olive mill wastewaters (OMWW) there are hardly papers dealing with pre-treatments of table olive processing wastewaters. The treatment of OMWWs has similar problems to those of the FTOP since polyphenols would inhibit their biological treatment. However, the OMWW conductivity is considerably lower and suspended solids and COD concentrations are much higher in comparison with the FTOP. The main characteristics of the OMWWs depending on the olive oil production method were reported by Azbar el al. [9] Paraskeva and Diamadopoulos [10] summarized the techniques used for OMWWs treatment. It is interesting to highlight that the COD removal efficiencies were lower than 50% using separated physico-chemicals treatments; thereby a process combination was necessary to enhance the treatment efficiency. In the last years, the adsorption has been reported as one the most promising OMWW pre-treatment in view of a further biological treatment. The adsorption achieve high polyphenol removal efficiencies [11], also it can use as a treatment before the use of OMWW for hydrogen photo-production [12]. Barbera et al. [13] studied

adsorption as the only treatment before the OMWW application to a particular agricultural purpose. Thus, these authors achieved a 95% of polyphenols removal with $80 \text{ g}\cdot\text{L}^{-1}$ of activated carbon.

Focusing on the FTOPs treatment, Segovia-Bravo et al. [14] studied the ozonation of fermentation brines with the aim of eliminating both polyphenols and microorganisms in order to reuse the brine. García-García et al. [15] proposed electro-coagulation as pre-treatment of a further biological process. According to the authors, most of the phenols in the wastewater from the table olive packaging industry were removed, what allowed treating the effluent in a biological process.

Thus, only a few papers have been found in the literature about the partial treatment of table olive processing wastewaters. It is evident that pre-treatments can be carried out either to eliminate polyphenols in view of a further biological treatment or to preserve them with the aim of applying a membrane process for their recovery. In this paper both possibilities are covered with the three pre-treatments studied: pH adjustment plus sedimentation, coagulation/flocculation plus sedimentation and adsorption.

VI.1.1.2. Materials and Methods

Wastewater

Fermentation brine was provided by a table olive packaging industry located in Comunidad Valenciana (Spain). Before its use, wastewater was stored at a temperature of 4°C .

Chemicals

HCl (6 N) y NaOH (10 M) solutions were prepared for pH adjustment. For the total phenols analysis hexane, ethyl acetate, methanol and sodium carbonate (Panreac) and Folin & Ciocalteu's reagent (Sigma Aldrich) were used. Table 1 and Table 2 show the different activated carbons (Chiemivall) and chemicals for coagulation-flocculation (Derypol) added in the adsorption and physico-chemical tests, respectively.

Table 1. Powder activate carbon.

Activate carbon	Characteristics	pH
Clarimex 061 CAE	Pinewood activated with phosphoric acid macroporous	2-4
Clarimex 061 GAE	Modified from CAE	4.5-6.5
BM8	Bituminous activated with water vapor micro-mesoporous	9-10
CCP80	Coconut shell activated with water vapor	9-11

Table 2. Coagulants and flocculants.

Coagulants		Characteristics	
GT-25		Vegetable Origin (Acacia)	
K-225		Synthetic. Suitable for secondary clarifier	
HA-89		Synthetic. Specific for cutting oils	
Flocculants	Characteristics	Ionic character	Molecular weight
ZW-332	Amphoteric	-	High
TG-325		Low	Very high
DR-3000	Cationic	Medium	High
DF-100		High	High
GO-2030	Anionic	High	Very high

Analyses

For the characterization study 20 samples were analysed by measuring pH, conductivity, turbidity, total phenols (T.Ph), sodium (Na^+), chloride (Cl^-), suspended solids (SS) and volatile suspended solids (VSS). The phenolic profile was analysed in six samples selected according to the measured total phenols concentration, in order to obtain the phenolic profile in samples with different total phenols content, including the maximum and minimum concentrations.

The pH and conductivity measurements were carried out with pH-Meter GLP 21+ and EC-Meter GLP 31+ (Crison), respectively. The turbidity was determined with a Turbidimeter D-112 from Dinko Instruments. The SS and SSV were measured according to APHA, 2005 [16]. The ions and the soluble COD concentrations were analysed by using kits and a Spectrophotometer DR600 (Hach Lange).

Phenol total content determination and HPLC analysis

For the polyphenols measurement, all samples were previously treated in order to extract them according to El-Abbassi et al. [17]. The extracts were brought to dryness in a rotary evaporator (Rotavapor R-114 from BÜCHI) at 40°C and the residue was dissolved in methanol. The extracts obtained were used for total phenols and UPLC-PDA analysis. Total phenols (simple phenolic and polyphenolic compounds) were measured spectrophotometrically according to the Folin-Ciocalteu method [18]. Results were expressed as ppm equivalent of tyrosol ($\text{mg TY} \cdot \text{L}^{-1}$). UPLC-PDA analysis were carried out on Waters Acquity UPLC system (Milford, MA, USA) equipped with a binary solvent manager, sample manager, column compartment, and 2996 PDA detector, connected to Waters Masslynx 4.1 software. The separation was carried out using a Waters BEH C18 column (2.1 × 100 mm, 1.7 μm) at 40 °C. The optimal chromatographic conditions were established: solvent system, phase A, 1 % formic acid in acetonitrile, and phase B, 1 % formic acid in water; gradient

conditions were as follows: 100% B at 0 min for 1 min to 55% A in 25 min, then 100% A at 30 min, held for 5 min, returned to 100% B in 2 min, and equilibrated for 3 min before the next injection; flow rate of $0.4 \text{ mL}\cdot\text{min}^{-1}$ and injection volume of $5 \mu\text{L}$. The samples (7 mg) were reconstituted in 1 mL of IS (hydroquinone at $0.5 \text{ mg}\cdot\text{mL}^{-1}$ in MeOH). External calibration curves were obtained for different analytes in different concentrations which were dissolved in the IS solution and injected in triplicate. Results were expressed as ppm of phenolic compound tested.

Jar tests

Jar test equipment was used both for mixing the neutralization chemicals in the pH adjusting experiments and for powder activated carbon and coagulation/flocculation experiments.

For all these tests, 500 mL of wastewater were poured in each beaker of a Flocumatic 4 jar-test apparatus from JP Selecta. In the pH adjustment tests, the range was between 2 and 11 and the temperature was 22°C . Chemicals were added at a stirring velocity of 150 rpm. Afterwards stirring was lowered to 60 rpm during 5 minutes in order to enhance floc formation. In the coagulation-flocculation tests, coagulants were added at 150 rpm (reaction time was 2 minutes for K225 and H89 and 8 min for the coagulant GT-25 according to provider recommendations). Temperature was maintained at 22°C . Then pH adjustment was performed for enhancing the effect of the flocculant. Afterwards flocculants were added and stirring was lowered to 60 rpm during 5 minutes. In the adsorption tests the reaction time ranged between 1 and 4 hours at 150 rpm. After the corresponding mixing phases the samples were settled during 90 minutes.

VI.1.1.3. Results and Discussion

Wastewater characterisation

Table 3 shows the mean values and the standard deviation calculated after the analysis of 22 FTOPs that were referred to as FTOP_i , where i is the number of the sample processed ($i = 1 - 22$).

It can be observed that the FTOP is acidic (pH around 4). Conductivity is very high, having an average value of $88 \text{ mS}\cdot\text{cm}^{-1}$ due mainly to the sodium chloride added for olives conservation. Suspended solids concentration is also high (around $1319 \text{ mg}\cdot\text{L}^{-1}$), what implies high turbidity values. Concerning organic matter, soluble COD value average for the 22 samples is $17.9 \text{ g}\cdot\text{L}^{-1}$ and the T.Ph concentration is $1045 \text{ mg TY}\cdot\text{L}^{-1}$. In comparison with olive mill wastewater (more widely studied), conductivity of FTOP is considerably higher, whereas the concentration of SS, soluble COD and pH value are lower.

Table 3. Wastewater characterization.

Physicochemical parameters	Contents
pH	4.0±0.1
Electrical Conductivity (mS·cm ⁻¹)	88±11
Turbidity (NTU)	328±128
Soluble COD (g·L ⁻¹)	17.9±4.1
Na ⁺ (g·L ⁻¹)	70.6±1.7
Cl ⁻ (g·L ⁻¹)	62.7±1.5
SS (mg·L ⁻¹)	1319±622
SSV (%)	53±7
Total Phenols (mg TY·L⁻¹)	1045±245

It has to be highlighted that the polyphenols concentration and the phenolic profile in the wastewater will depend on the cultivar, the degree of ripeness and the duration of the three phases of the table olives production (debitting, rinsing and brining). The results of the analysis of the phenolic profile indicated that hydroxytyrosol (HTY) and tyrosol (TY) were present in the FTOP wastewater. However, other polyphenols were not detected. These results are in agreement to those reported by Charoenprasert and Mitchell [19]. These authors concluded that for the Spanish-Style green olives processing, oleuropein is cleaved in the debittering stage, what drives to hydroxytyrosol and oleoside-1-methyl ester. Meanwhile hydroxytyrosol is stable, oleoside-1-methyl ester concentration decreases rapidly due to the conversion to elenolic acid and glucose. On the other hand, tyrosol is formed from the ligstroside hydrolysis. These results are also similar to those reported by García-García et al. [15], who only identified HTY and TY and their glucosides in the FTOP fermentation brines. For all characterized FTOP, HTY was the polyphenol with the highest concentration. Its concentration varied between 263 and 880 mg HTY·L⁻¹ for the FTOPs with 885 mg TY·L⁻¹ and 1536 mg TY·L⁻¹ of the T.Ph concentration, respectively. These were the maximum and minimum concentrations measured in 22 FTOPs analysed. Tyrosol concentrations varied between 45 and 132 mg TY·L⁻¹, for the same samples. However, in the literature different results can be also found. Parinos et al. [20] reported only 76 mg·L⁻¹ of T.Ph in the fermentation brine from the Spanish-Style green olives processing. These authors reported that the most concentrated polyphenol was dibutyl phthalate and the concentration of HTY was lower than 10 mg·L⁻¹.

Wastewater pre-treatments

Different wastewater samples were used during the experiments. However, for a better comparison among the different tested pre-treatments, a final series of experiments with the same wastewater sample was performed (FTOP₂₀). FTOP₂₀ was characterized by pH = 4, conductivity = 73.7 mS·cm⁻¹, soluble COD = 14.2 g·L⁻¹, SS = 971 mg·L⁻¹, turbidity = 186 NTU, T.Ph = 885 mg TY·L⁻¹, HTY = 263 mg HTY·L⁻¹ and TY = 45 mg TY·L⁻¹.

pH adjustment and sedimentation

Figure 1 shows FTOP₂₀ treatment efficiency in terms of SS, soluble COD, turbidity and T.Ph removal. It is observed that when FTOP₂₀ pH was increased or decreased, from the original pH of the sample (pH = 4), turbidity was reduced. The highest turbidity reduction was achieved at pH 10 and 11 with 95% and 97 % of turbidity removal, respectively. As expected, SS concentration followed the same tendency as turbidity (42% SS removal was obtained at pH = 10 and 45% at pH = 11).

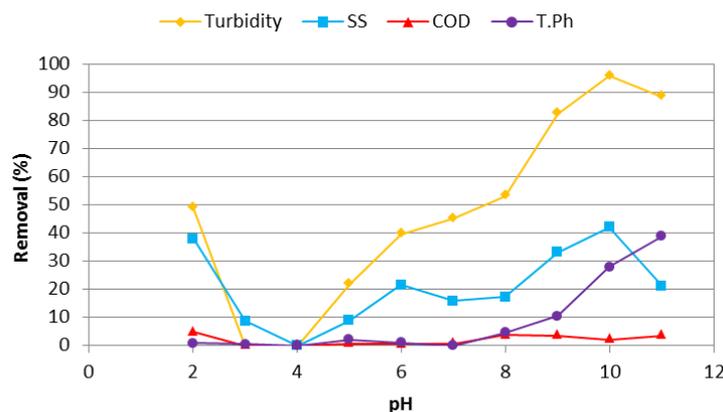


Figure 1. Removal percentage of turbidity, SS, soluble COD and T.Ph in FTOP₂₀ after pH adjustment and sedimentation tests.

Concerning the phenolic compounds, no variation was observed up to pH values of 8. Above pH = 8, T.Ph removal was increasing. Thus, at pH = 11 phenols removal was 39% (it was the highest removal efficiency). This reduction can be explained by hydroxytyrosol oxidation. Oxidation did not occurred in the storage tank of the fermentation brine due to the anaerobic conditions [21]. Finally, soluble COD was not eliminated as expected. Above pH = 8 a slight reduction was achieved due to phenols removal.

Coagulation-Flocculation

In the first jar-tests series, all the flocculants were tested with every coagulant. Initial coagulant and flocculant concentrations (1000 and 30 mg·L⁻¹, respectively) were recommended by the chemicals supplier in view of the wastewater characteristics. The turbidity was measured at every test with the aim of selecting the best coagulant/flocculant. This test was performed with FTOP₈ (turbidity = 181 NTU). Figure 2 illustrates the turbidity achieved after treatment.

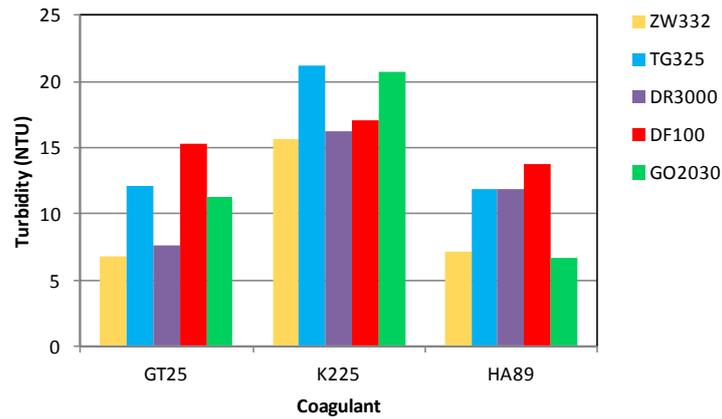


Figure 2. FTOP₈ turbidity after pre-treatment with three coagulants (1000mg·L⁻¹) and five flocculants (30 mg·L⁻¹).

It is observed that the lowest turbidity values were obtained for GT25 and HA89 coagulants. For GT25 coagulant the minimum turbidity (6.8 NTU) was obtained in combination with ZW332 flocculant (96.3% of turbidity reduction was achieved). For HA89 coagulant, GO2030 and also ZW332 flocculants yielded the highest turbidity reductions with 96.3 and 96.1%, respectively.

Once GT25 and ZW332 were selected, further jar-tests were carried out to determine the most appropriate concentrations. In the second test series, different amounts of GT25 (between 100-2000 mg·L⁻¹) were tested with ZW332 (30 mg·L⁻¹). This test was performed with FTOP₉ (turbidity = 328 NTU). Figure 3 illustrates these results.

The highest turbidity reduction (86.6%), involving the minimum chemicals concentration, was for 800 mg·L⁻¹ of GT25 and 30 mg·L⁻¹ of ZW332. For these concentrations, the jar-tests experiments varying pH (from 2 to 11) were performed with FTOP₂₀.

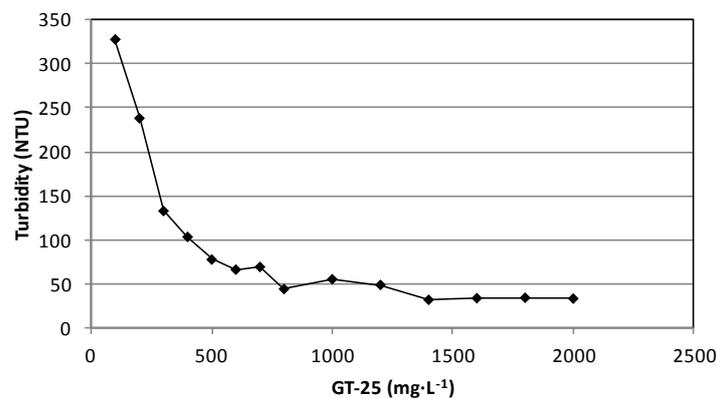


Figure 3. FTOP₉ turbidity after pre-treatment with GT25 (between 100-2000 mg·L⁻¹) + ZW332 (30 mg·L⁻¹).

Figure 4 shows the treatment efficiency in terms of SS, soluble COD, turbidity and T.Ph removal.

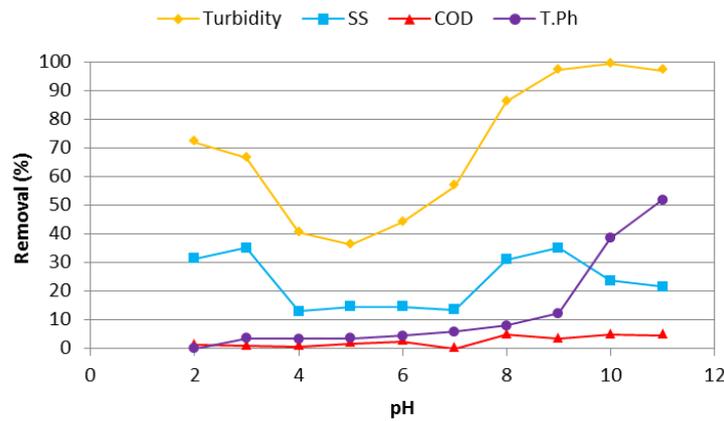


Figure 4. Removal percentage of turbidity, SS, soluble COD and T.Ph after pre-treatment with GT25 ($800 \text{ mg}\cdot\text{L}^{-1}$) + ZW332 ($30 \text{ mg}\cdot\text{L}^{-1}$) for different pH.

The pollutants removed in the tests at different pH values in the coagulant/flocculant treatment, showed a very similar behaviour to that observed in the pH adjustment/sedimentation tests. Turbidity was reduced by either increasing or decreasing pH of FTOP₂₀. The maximal turbidity reduction was 99.3% at pH = 10. The SS removal efficiencies remained constant (around 14%) between pH 4 to 7. The maximal removal efficiencies were at pH = 3 and pH = 9, in both cases around 35%. The low SS reduction, in comparison with the high turbidity removal efficiency, can be due to the low size and density of the SS. König et al. [22] obtained similar values in turbidity and COD removal efficiencies treating pickle wastewater with $8.2 \text{ g}\cdot\text{L}^{-1}$ of chloride concentration with organoclays as flocculant. The removal efficiency of SS reported by these authors ranged between 59 and 73%.

Concerning the T.Ph, chemicals enhanced their elimination to above pH 8, due to their adsorption on the formed flocs in addition to hydroxytyrosol oxidation. At pH = 11, 51.9 % of T.Ph were eliminated, what also implied a certain soluble COD reduction.

Powder activated carbon (PAC) adsorption

The aim of the PAC addition was to eliminate polyphenols in the FTOP in order to avoid an inhibitory effect in a further biological treatment. It has to be commented that a further PAC separation from the treated wastewater was necessary. This operation would also eliminate a part of the SS. However, this study was focused on polyphenols and COD removal.

Adsorption is an appropriate process to separate the phenolic compounds from the wastewaters [23]. The use of acid cracking plus granular activated carbon adsorption was studied by Farabegoli et al. [24] previous to the biological treatment of olive mill wastewater (OMW). These authors reported that this pre-treatment enhanced the phenols removal in the biological reactor.

In our work, it was tried to separate partially phenolic compounds in order to pre-treat FTOP wastewater in view to a further biological treatment. The FTOP contains a great variety of organic compounds, including substances that also can be removed by adsorption together with the polyphenols. The acidic pH in the FTOP favours the phenols adsorption onto the activated carbon [25, 26]. This can be explained by the predominance of the anionic form [27] of the polyphenols in alkaline solutions, increasing the repulsion forces between phenol molecules and activated carbon, since PAC is also charged negatively at the alkaline pH values [28].

Table 4 shows the T.Ph removal efficiencies with the four tested PACs. The first test was performed with FTOP₁₅ (18.5 g·L⁻¹ of soluble COD and 1391 mg·L⁻¹ of T.Ph concentration). The PAC concentration was 4 g·L⁻¹ and the reaction time were 4 hours. The highest polyphenols removal was achieved by BM8 (66.9 %), followed by CCP80 (57.5 %). This was due to the PACs pore size. Mesoporous or microporous in the activated carbons are more appropriate than macroporous ones for the removal of low molecular weight polyphenols. Additionally, the phenolic compounds of the FTOP are weak acids whose separation is enhanced by alkaline functional groups on the PAC surface [29].

Table 4. Total phenols removal efficiencies in the adsorption test with FTOP₁₅ and 4 g·L⁻¹ PAC concentration (4h reaction time).

PAC	T.Ph removal (%)
Clarimex 061 CAE	49.8
Clarimex 061 GAE	33.8
CCP80	57.5
BM8	66.9

The aim of the second tests series was to determine the time required in the phenols adsorption with BM8, for reaching the equilibrium concentration in the wastewater. For it, different amounts of BM8 (2, 4 and 6 g·L⁻¹) were mixed with FTOP₁₉ (14.1 g·L⁻¹ of soluble COD and 929 mg TY·L⁻¹ of T.Ph concentration) and the T.Ph concentration was analysed after 10, 15, 20, 30, 45, 60 and 120 minutes. Figure 5 shows these results. It can be observed that the T.Ph adsorption was fast, since in the first 15 minutes most of polyphenols were adsorbed. From 60 minutes on, the T.Ph concentration in FTOP₁₉ for all tests, remained practically constant. Thus, the equilibrium adsorption time for BM8 was 60 minutes and the T.Ph removal efficiencies in equilibrium were around 30%, 63% and 75% for 2, 4 and 6 g BM8·L⁻¹, respectively.

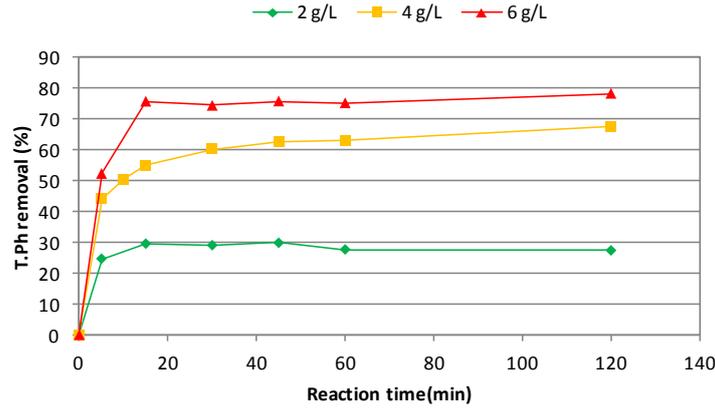


Figure 5. Total phenols percentage removal in FTOP₁₉ after PAC pre-treatment with 2 g·L⁻¹, 4 g·L⁻¹ and 6 g·L⁻¹ of BM8.

Isotherms representation leads to a better understanding of the adsorption process. Langmuir assumes a uniform surface and a single layer of adsorbed material [30] unlike Freundlich isotherm that assumes that adsorption is heterogeneous and there is not only a layer of adsorbed material [31]. The linear form of both isotherms equations are the following:

$$\text{Langmuir; } \frac{C_e}{q_e} = \frac{1}{K_L \cdot q_0} + \frac{1}{q_0} \cdot C_e \quad \text{Eq. (1)}$$

$$\text{Freundlich; } \ln q_e = \ln K_f + \frac{1}{n} \cdot \ln C_e \quad \text{Eq. (2)}$$

where C_e (mg·L⁻¹) is the T.Ph concentration at equilibrium, q_e (mg·g⁻¹) is the T.Ph mass adsorbed at equilibrium per g of BM8, q_0 (mg·g⁻¹) is the maximal adsorption capacity and K_L (L·mg⁻¹) is Langmuir coefficient. In Freundlich equation, n and K_f (mg·g⁻¹)·(mg·L⁻¹)^{-1/n} are both empirical coefficients. K_f indicates the adsorption capacity and n is related with the adsorption intensity. Thus, n higher than 1 means that the operating conditions are appropriate for the adsorption process [32, 33].

Figure 6 and Figure 7 show Langmuir and Freundlich isotherms for FTOP₂₀, respectively.

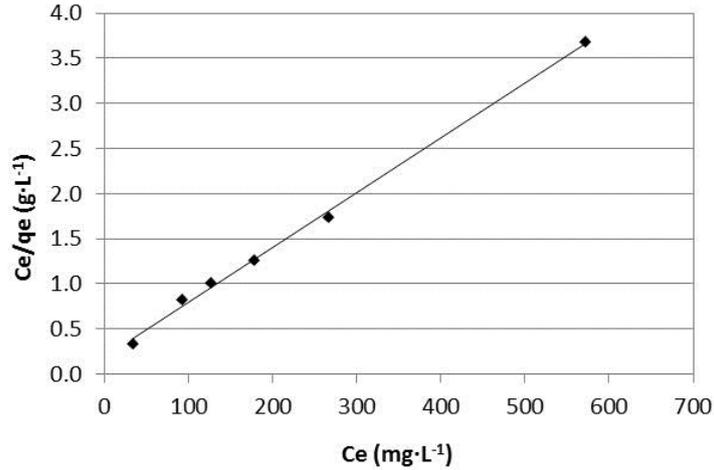


Figure 6. Langmuir isotherm for FTOP₂₀ (22°C).

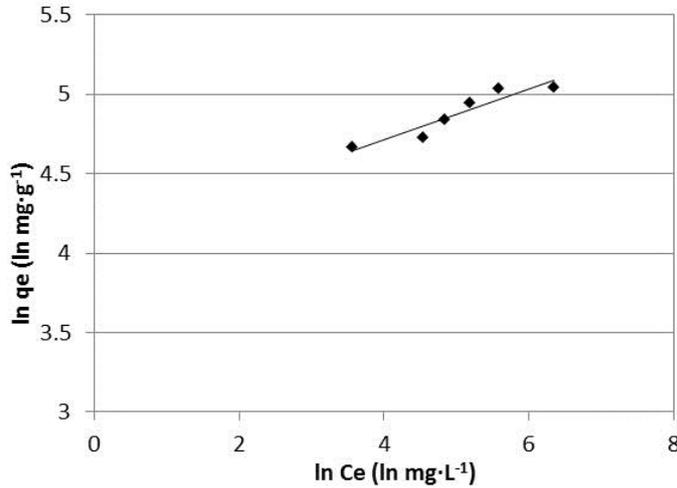


Figure 7. Freundlich isotherm for FTOP₂₀ (22°C).

The data obtained from the adsorption tests fitted to Langmuir equation was better than to Freundlich equation ($R^2 = 0.9973$ vs 0.8854). For Langmuir isotherm the calculated coefficients were: $q_0=163.934$ ($\text{mg}\cdot\text{g}^{-1}$) and $K_L=0.033$ ($\text{L}\cdot\text{mg}^{-1}$).

It has to be commented that the carbon is not a selective material for the adsorption. It means that the materials retained onto the PAC were not only polyphenols, also other organic compounds of the wastewater were adsorbed. For this reason, it was considered that tests had to be replicated with other FTOP, which containing more COD and T.Ph concentrations. In this way, FTOP₂₂ was analysed (21.5 $\text{g}\cdot\text{L}^{-1}$ for soluble COD and 1549 $\text{mg TY}\cdot\text{L}^{-1}$ for T.Ph concentration). Figure 8 shows comparatively Langmuir isotherms for FTOP₂₀ and FTOP₂₂. It can be observed that all the data, considering both samples, fit to a straight line and the coefficient values were $q_0=175.439$ ($\text{mg}\cdot\text{g}^{-1}$) and $K_L=0.022$ ($\text{L}\cdot\text{mg}^{-1}$) with $R^2=0.9954$.

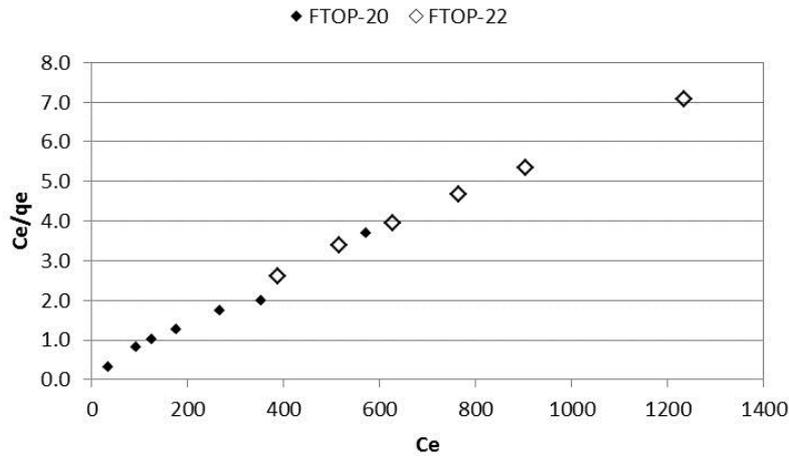


Figure 8. Langmuir isotherm for FTOP₂₀ and FTOP₂₂ (22°C).

VI.1.1.4. Conclusions

After characterizing 22 FTOPs samples, it can be concluded that their high conductivity (around $88 \text{ mS}\cdot\text{cm}^{-1}$), total phenols concentration (between 885 and $1536 \text{ mg TY}\cdot\text{L}^{-1}$) and values of suspended solids and turbidity (around $1319 \text{ mg}\cdot\text{L}^{-1}$ and 328 NTU , respectively) make very difficult their treatment. Thus, the selection of an appropriate pre-treatment is of paramount importance for the achievement of a successful final FTOP management.

The pre-treatment selection will depend on the final FTOP management. If no polyphenols elimination is required, in view of a further recovery (e.g. integrated membrane treatment for polyphenols recovery), the pH adjustment ($\text{pH} = 9$) and coagulation/flocculation at pH value of 9 are the best pre-treatments. For this pH conditions, both pre-treatments did only eliminate 10% of polyphenols. Also, the SS and turbidity removal efficiency with and without coagulant/flocculant addition were 35.0% and 33.1% and 97.2% and 82.5%, respectively. These results show that the coagulation/flocculation chemicals slightly improved the pollutants removed. So, this little increases in the efficiency not enough to support the higher costs.

However, if the final FTOP treatment is the biological oxidation, the adsorption with PAC would be a treatment to be considered since high polyphenols removal efficiencies are achieved, what implies to reduce the biomass inhibition in the biological process. In the present work, the maximum amount in the T.Ph and soluble COD removal were 96.0% and 21% with $8 \text{ g}\cdot\text{L}^{-1}$ of BM8. Besides, the PAC pre-treatment would enable to maintain the T.Ph concentration in feeding wastewater (increasing or decreasing the amount of BM8), in spite of variations of this parameter in FTOP samples.

VI.1.1.5. References

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