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Flocculation on the Treatment of Olive Oil Mill Wastewater: Pretreatment

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***Abstract*—**Currently, continuous two-phase decanter process used for olive oil production is the more internationally widespread. The wastewaters generated from this industry (OMW) are a real environmental problem because of its high organic load. Among proposed treatments for these wastewaters, advanced oxidation technologies (Fenton, ozone, photoFenton, etc.) are the most favourable. The direct application of these processes is somewhat expensive. Therefore, the application of a previous stage based on a flocculation-sedimentation operation is of high importance. In this research five commercial flocculants (three cationic, and two anionic) have been used to achieve the separation of phases (liquid clarified-sludge). For each flocculant, different concentrations (0-1000 mg/L) have been studied. In these experiments, sludge volume formed and the final water quality were determined. The final removal percentages of total phenols (11.3-25.1%), COD (5.6-20.4%), total carbon (2.3-26.5%), total organic carbon (1.50-23.8%), total nitrogen (1.45-24.8%), and turbidity (27.9-61.4%) were determined. The variation on electric conductivity reduction percentage (1-8%) was also determined. Finally, the best flocculants with highest removal percentages have been determined (QG2001 and Flocudex CS49).

***Keywords*—**Flocculants, flocculation, olive oil mill wastewater, water quality.

I. INTRODUCTION

THE intensive activities of industry are accompanied by many types of wastewaters which contribute to the depletion of environmental quality. In this sense, enormous quantities of industrial wastewaters are discharged into natural water bodies. Industrial wastewaters are mostly loaded with high organic matter [1]. In order to decrease the organic matter content in the wastewaters, it is necessary to treat wastewaters before their discharge. The most commonly used treatments are pretreatment, primary, secondary or biological, and tertiary treatments. In the case of industrial wastewaters, the treatment was based on oxidation/reduction and a neutralization followed by a chemical precipitation [2].

In Spain, the main olive oil worldwide producer, there are more than 1700 olive oil factories, which gave rise to more than 1,54 million of tons of virgin olive oil during the 2010 campaign [3]. Olives and olive oil production grows year by year, implying a proportional increase in the volumes of wastewater generated (OMW). An average-sized olive oil factory produces 10–15 m^3/day of OMW. These wastewaters are characterized by low pH, extremely high concentration of suspended and dissolved solids as well as heavy organic load. On the other hand, the high concentration of phenols and tannins commonly present in this effluent confers OMW phytotoxic and antimicrobial properties and low biodegradability [4], [5].

OMW must be treated before its disposal according to the present-day European environmental rules. Advanced oxidation processes (AOPs) involve the generation of highly reactive radical species, mainly hydroxyl radicals [6]. Hydrogen peroxide has been used to reduce BOD, COD, offensive odour and foaminess in domestic or industrial wastewaters for many years. Hydrogen peroxide treatment can be used as an autonomous treatment or as an improvement of existing physical or biological treatment processes, according to the situation. Nieto et al. [6], [7] have shown the advantages of chemical oxidation in the treatment of OMW: (i) high efficiency, (ii) simplicity, (iii) lack of residues and (iv) ability to treat many different compounds. In addition, it can be used as a pre-treatment stage before a biological step in order to increase the biodegradability of the recalcitrant compounds and thus lower the toxicity of these effluents [8]. The extension of wastewater treatment processes based on chemical oxidation is constrained by the cost of the process. This implies the need to include a pretreatment step (flocculation-sedimentation) to remove a portion of the organic load, and thus reduce operating costs.

Coagulation/flocculation is a commonly used operation in water and wastewater treatment in which compounds such as alum ($Al_2(SO_4)_3 \cdot 16\ H_2O$), aluminium chloride ($AlCl_3$), ferric chloride ($FeCl_3 \cdot 6\ H_2O$) and/or polymer are added to wastewater in order to destabilize the colloidal materials and cause the small particles to agglomerate into larger settleable flocs [9], [10]. Several studies have reported the examination of this process for the treatment of industrial wastewater, especially with respect to performance optimization of coagulant/flocculant, determination of experimental conditions, assessment of pH and investigation of flocculant addition [11], [12].

In this work, the introduction of flocculation as a pretreatment step for the olive oil mill wastewater was studied. Therefore, it studied the influence of different concentrations of flocculants in solid-liquid separation and flocs formation. Moreover, water quality and the reduction of the organic load were determined. Finally, the best flocculant to use was established.

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II. MATERIALS AND METHODS

A. Characterization of Olive Oil Mill Wastewater (OMW)

Wastewater samples were collected from several olive oil mills in the Andalusian provinces of Seville (Spain), operating with different trademarks olive-cleaning and vertical-centrifugation equipment's. The wastewaters used have been collected from storage ponds of each mill, in April after the 2013/2014 campaign. In other words, wastewaters taken correspond to waters from washing oil, washing olives, cleaning and other wastewaters collected from the activities of the mill.

Each wastewater was analysed and characterized. pH, moisture and volatile matters, total solid, organic matter, ash, chemical oxygen demand (COD), total carbon (TC), total organic carbon (TOC), inorganic carbon (IC), total nitrogen, NO_2+NO_3, electric conductivity, turbidity, total phenolic compounds, chloride, sulphate, electric conductivity, total iron and phenols were determined.

B. Experimental Conditions and Procedure

The developed oxidation process [2] consists of the following operations: chemical oxidation, neutralization, solid-liquid separation and filtration (Fig. 1).

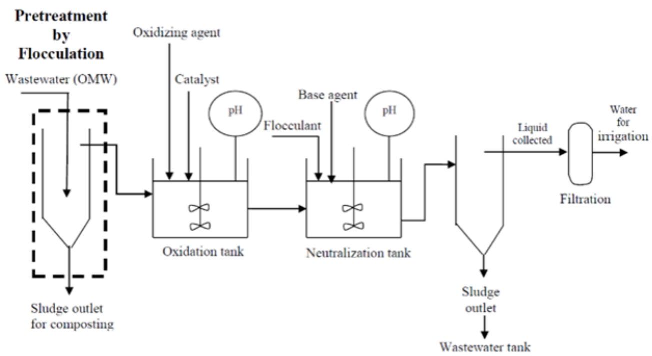

Fig. 1 Schematic diagram of the oxidation process used to produce irrigation water from olives and olive-oil-washing wastewaters.

With the aim to reducing the costs of the treatment process, an initial flocculation stage, at laboratory scale as pretreatment, was studied. In this step, different commercial flocculants were applied to remove the organic load.

C. Flocculation/Sedimentation Operation

The flocculation stage seeks the elimination of suspended solids, turbidity and colour. Tests were performed in a 1 L Imhoff cone. Volume occupied by solids (sludge) was recorded during time. In all tests the natural pH of OMW was not modified. For each flocculant the optimal dose was determined. The proposed flocculants had been chosen after a review of options offered by the market, considering their effectiveness at low concentrations, increasing speed sedimentation without modifying the properties of clarified water.

Mixture of flocculant with treated wastewater was carried out in two stages. In the first, mixing was strong (strong stirring at a constant speed of 700 rpm) but brief (short time equal to 1 min). This facilitates the uniform dispersion of the flocculant and promotes particles collisions. In a second stage, agitation was greatly reduced (375 rpm during 30 min [13]), keeping the flocs in suspension and movement, avoiding their disintegration and favouring their growth, and thereafter, the sample was left to settle for 150 min.

D. Flocculants

Cationic polyelectrolytes (organic polymer) with high molecular weight, soluble in water and based on polyacrylamide Flocudex (CS/45, CS49 and CS51) were purchased by Lamirsa Company, Terrassa (Spain). Anionic polyelectrolyte QG-2001 was provided by Gedar Andalusian Company, Granada (Spain). Other, anionic polyelectrolyte oil-based (Nalco-9913) was purchased from Nalco Española S.A., Barcelona (Spain). Table I shows the technical characteristics of these flocculants.

TABLE I
TECHNICAL CHARACTERISTICS OF FLOCCULANTS

Parameter	Flocudex			Nalco 9913	QG-2001
	CS/45	CS/49	CS/51		
Character	Cationic	Cationic	Cationic	Anionic	Anionic
Charge density	High	High	High	High	High
Physical state	Granular	Granular	Granular	Granular	Powder
Colour	White	White	White	White	White
Odor	None	None	None	None	None
pH, sol. 5 g/L		2.5-4.5	2.5-4.5		
Granulometry (mm)			1.25		
Apparent density (g/cm^3)		0.8	0.8	1.25	0.75
Viscosity sol. 5 g/L (cps)		500	700		1800
Solubility in water	Limited	Limited	Limited	Complete	Limited

E. Analytical Methods

pH value was measured by using CRISON pH meter, mod. LPG 22.

Moisture content was determined according to the weight loss of the sample after being placed in an oven at 105 ºC until reaching constant weight. The difference in weight with respect to the original sample, expressed in percentage, determined the moisture content.

Total solids were calculated by subtracting between 100 and the moisture.

Ashes correspond to the mineral salts remaining after sample incineration at 575 ºC for 3 h.

Organic matter is obtained by the difference between total solids and ash.

Electric conductivity was assessed using a CRISON conductivity meter, mod. Basic 30.

Turbidity was determined directly by using a HANNA turbidity meter, mod. HI93703.

Chemical oxygen demand (COD) was determined by the photometric determination of the concentration of chromium (III) after 2 h of oxidation with potassium dichromate/sulfuric acid/silver sulfate at 421K (German standard methods DIN 38 409-H41-1 and DIN ISO 15 705-H45).

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All iron ions were reduced to iron ions (II). These, with thioglycolate medium, form a reddish-purple complex with a derivative of triazine, which was determined photometrically at 565 nm (Standard methods ISO 8466-1 and German DIN 38402 A51).

Sulphates and chloride were determined photometrically (Standard German methods ISO 8466-1 and DIN 38402 A51).

The total phenols and phenol derivatives reacted with a derivative thiazol, giving purple azo dyes which were determined photometrically at 475 nm (Standard German methods ISO 8466-1 and DIN 38402 A51).

Finally, total carbon (TC), total organic carbon, inorganic carbon, total nitrogen, and NO_3+NO_2 were determined by using a Skalar total carbon and nitrogen analyzer, mod. Formacs^{HT} total and Formacs^{TN}.

III. Results and Discussion

A. Characterization of Olive oil Mill Wastewaters

In Table II it can see the characterization of the wastewaters used and obtained from accumulations rafts of different industries. In all cases, high values of turbidity, electric conductivity, chlorine, phenolic compounds, COD, TC and TOC were determined.

Sampling was conducted two months after the end of olive harvest campaign which allowed a natural precipitation. So accumulation rafts have two phases: solid (lower part) and liquid (upper part). The wastewaters used in this study were obtained from liquid phase of the rafts.

TABLE II
Characterization of Olive Oil Mill Wastewater

Parameter	Sev-1	Sev-2	Sev-3
pH	8.5	8.6	8.8
Moisture and volatile matters, %	97.7	88.6	99.1
Total solids, %	2.32	11.4	0.95
Organic matter, %	0.32	1.8	
Ash, %	2.01	9.6	
COD, mg O_2/L	6187	18537	24302
Total carbon, mg/L	2636	14077	16077
Total organic carbon, mg/L	1891	11561	13371
Inorganic Carbon, mg/L	746	2516	2706
Total nitrogen, mg/L	113	390	376
NO_3+NO_3, mg/L	Trace	Trace	Trace
Conductivity, mS/cm	31.1	167	183
Turbidity, FTU	322	997	885
Total phenols, mg/L	37.8	190	179
Total Iron, mg/L	7.04	42.3	111
Cl, mg/L	10033	11544	12025
SO_4, mg/L	3922	1299	1299

B. Volume of Sludge and Water Collected

The high organic load of the wastewater does not allow obtaining treated water at the outlet of the oxidation reactor that meets the standards requisites required by the authorities.

But inserting a settling unite prior to oxidation reactor is a key step to achieve the required water treated values. So, a rapid phase's separation and the formation of a large volume of liquid phase in a short time (in presence of flocculant) allow using a decanter with small surface. This fact allows achieving and maintaining the desired flow of treated water during the process.

Fig. 2 illustrates the rate of sludge formation volume (volume of solid occupied), V = f(t), during the flocculation operation for different concentrations of Flocudex CS/45 flocculant.

A small addition of Flocudex CS/45 (5 mg dm^{-3}) significantly improves the phase separation, increasing the sludge volume to 11 cm^3 (Fig. 2).

Increasing flocculant doses from 5 to 400 mg/L does not imply an increase in the volume of sludge formed (Fig. 2).

In Fig. 3 it can be observed the maximum sludge volume formed by each flocculant and the flocculant doses used. Nalco 9913 and Flocudex CS51 registered the major sludge volume formed at 200 mg/L and 100 mg/L respectively.

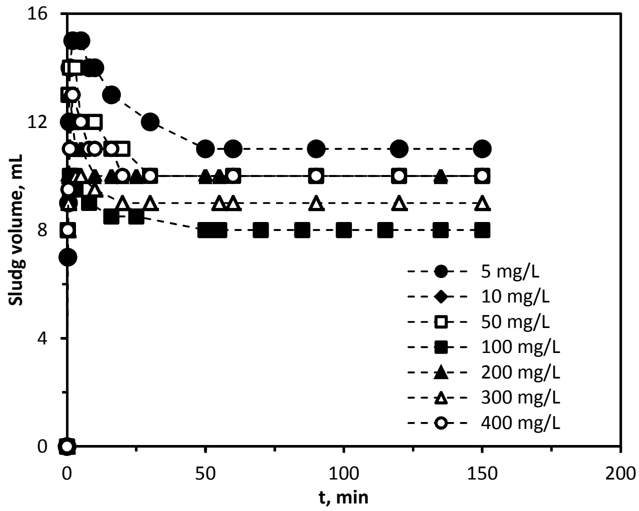

Fig. 2 Dynamic behaviour of sludge volume formed during flocculation with different concentration of Flocudex CS/45

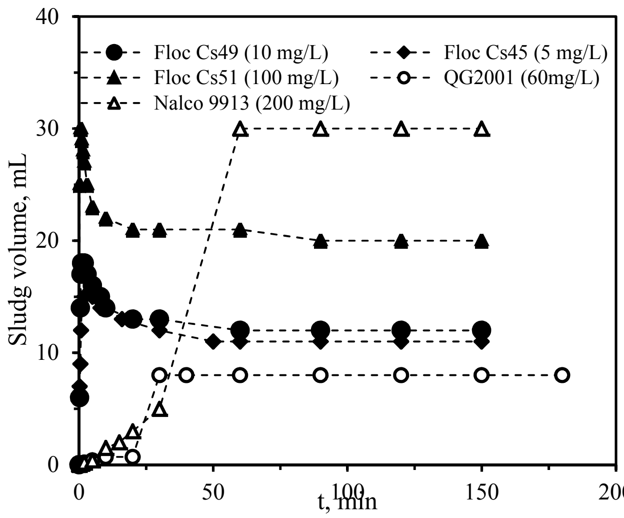

Fig. 3 Dynamic behaviour of sludge volume formed by all flocculants at the best flocculant doses.

C. Wastewater Quality after Flocculation-Sedimentation Operation

In all flocculation test realized, the wastewater composition before and after flocculation was determined. The parameters determined were pH, electric conductivity, turbidity, total phenols, COD, TC, TOC, and TN.

The comparison among the initial pH of OMW and the final pH obtained after flocculation can be seen in Fig. 4. It has been registered a decrease in the final pH values of the wastewater by the three cationic flocculants type Flocudex (CS45, CS49, and CS51). However, the two other anionic flocculants (Nalco 9913 and QG2001) have registered an increase of pH values of the final wastewater obtained. This fact can be explained by considering an ion exchange between the organic matter of OMW and flocculants with H^+ and OH^- releasing.

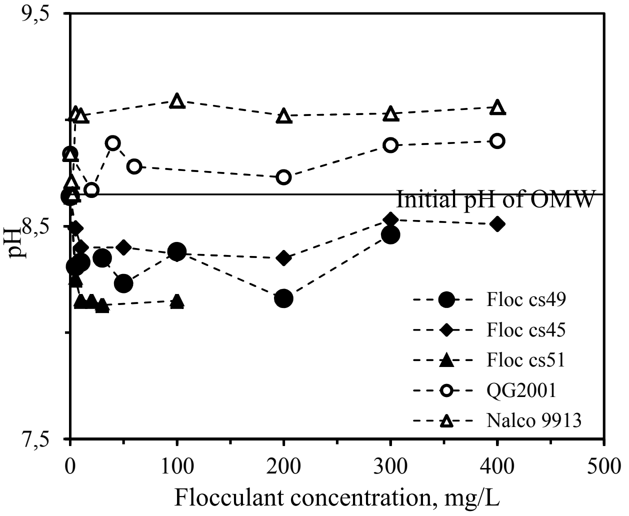

Fig. 4 pH variation on the OMW treated by flocculation

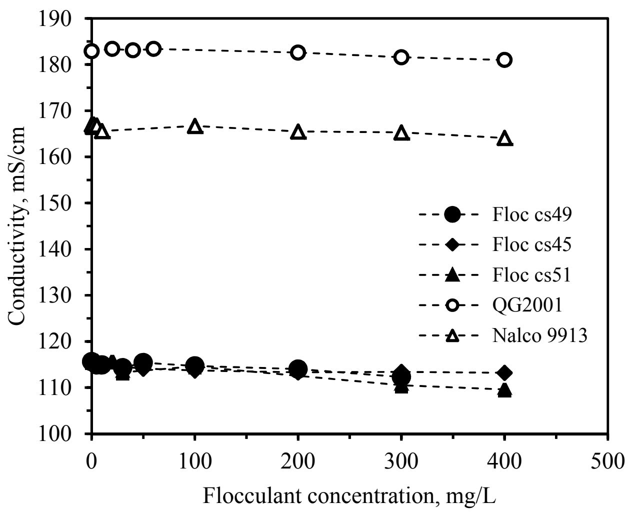

Fig. 5 Conductivity variation on the OMW treated by flocculation

In all experiments, flocculation performed a slight decrease (1-8%) in the values of the electrical conductivity (Fig. 5). This fact is due to the elimination of the sodium ions present in the wastewaters (because NaOH was used in cleaning tanks on the olive oil factory).

In all flocculation tests a significant decrease in turbidity value was observed. These values were varied among 33.6% (for QG2001) and 61.4% (Flocudex CS49) of turbidity removal (Fig. 6).

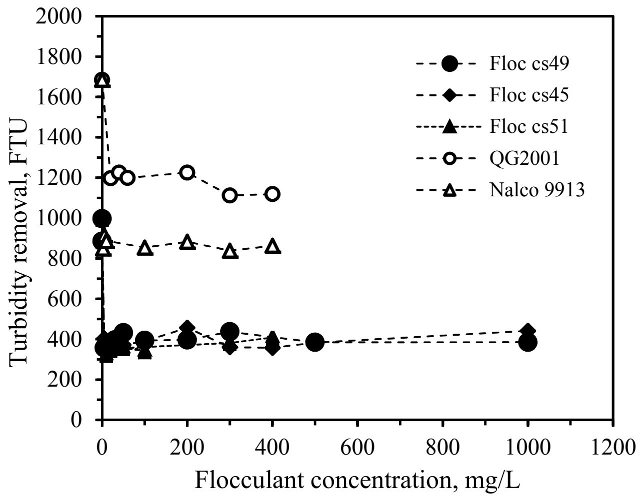

Fig. 6 Turbidity removal for different flocculants used

In Fig. 7 it can be seen the COD removal registered by each flocculant at different concentrations. In all cases the elimination of COD was detected, and the COD removal was varied between 5.6% and 20.4%. The best flocculants have been QG2001 and Flocudex CS49 with 20.4% and 16.0% of COD removal, respectively.

The elimination of the total phenolic compounds by flocculants was instantaneous in the case of all cationic flocculants type Flocudex (CS45, CS49 and CS51). However, the removal of total phenols was proportional to the dose of flocculant used, in the case of anionic flocculants Nalco 9913 and QG2001 (Fig. 8).

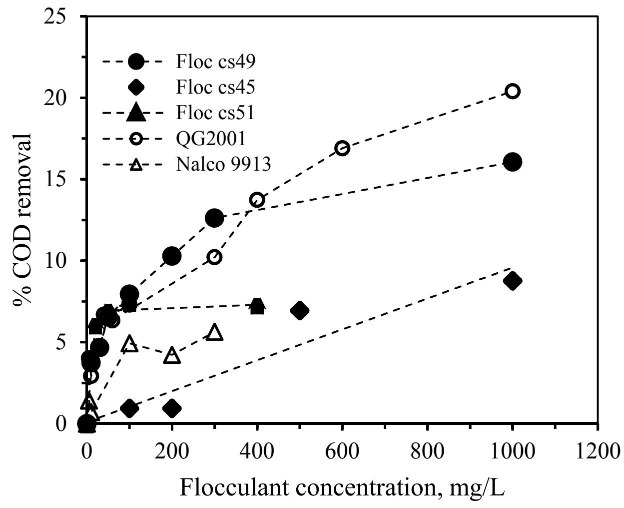

Fig. 7 COD removal by flocculants at different concentrations used.

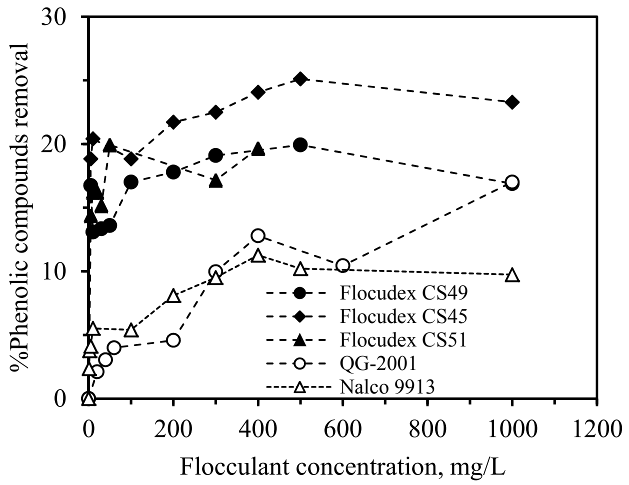

Fig. 8 Total phenolic compounds removal by each flocculant at different doses used.

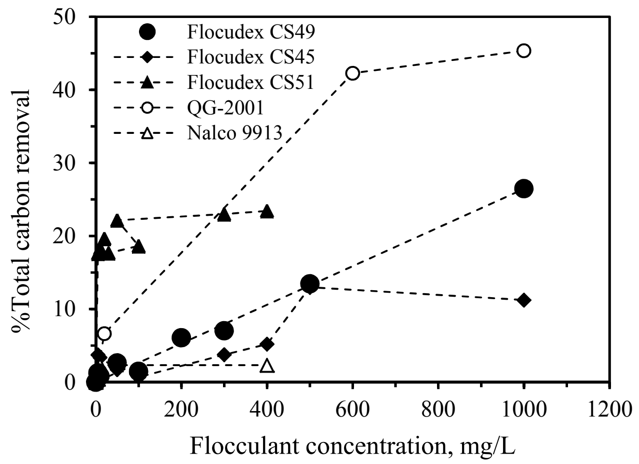

Fig. 9 Total carbon removal determined by each flocculant at different concentrations used

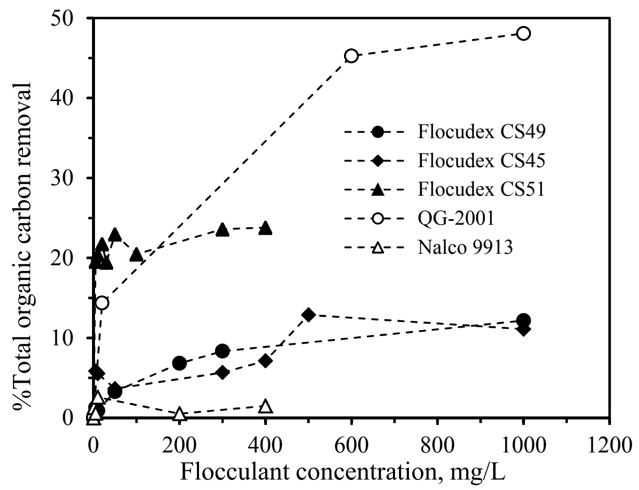

Fig. 10 Total organic carbon removal determined for each flocculant at different concentrations used

In Fig. 9, it can be observed the total carbon removal behaviour by each flocculant at different flocculant concentrations. In the case of Flocudex CS49, the total carbon removal was increased linearly with the augmentation of flocculant concentration. The major values of TC removal were registered in the case of flocculants Flocudex type CS49, CS51 and QG-2001.

In the case of TOC removal, similar results were observed to that determined for TC. The highest removal values determined for QG-2001, Flocudex CS49 and Flocudex CS51 were 48.1%, 11.1%, and 23.8%, respectively (Fig. 10). However, the highest values of TN removal for Flocudex CS51 (23.5%), Flocudex CS45 (22.0%), and Flocudex CS49 (12.8%) were determined, Fig. 11.

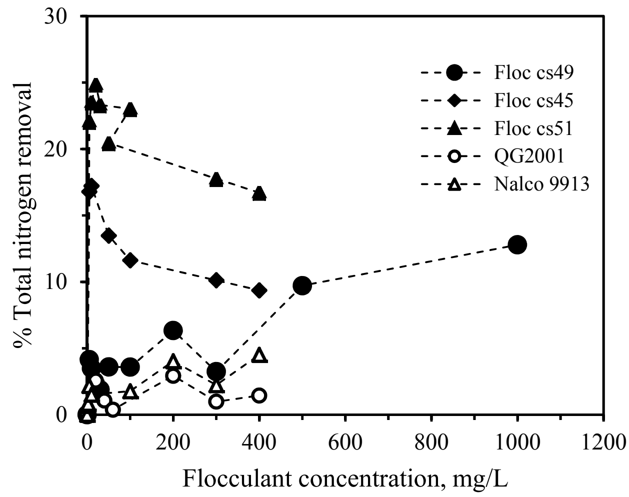

Fig. 11 Total nitrogen removal determined for each flocculant at different concentrations used.

IV. Conclusion

Commercialization of advanced oxidation technologies is limited by the costs of treatment. Mainly, operating costs (energy and chemical reagents costs). This fact implies that the application of a pretreatment step by flocculation (COD removal = 5.6-20.4%) is a must in the treatment processes based on the non-conventional methods.

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References

[1] N. Trgo, N. V. Medvidović, and J. Perić, "Application of mathematical empirical models to dynamic removal of lea don natural zeolite clinoptilolite in a fixed bed column," *Indian J. Chem. Technol.* 8, 2011, 123-131.

[2] L. M. Nieto, G. Hodaifa, S. R. Vives, J. A. Casares, and J. Ochando, "Degradation of organic matter in olive-oil mill wastewater through homogeneous Fenton-like reaction," *Chem. Eng. J.* 173, 2011, 503-510.

[3] FAOSTAT, "Website of Food and Agriculture Organization of the United Nations, 2012,"http://faostat.fao.org/.

[4] S. E. Garrido Hoyos, L.M. Nieto, F.C. Rubio, and A.R. Cormenzana, “Kinetics of aerobic treatment of olive mill wastewater (OMW) with *Aspergillus terreus*,”*Process Biochem*. 37(10), 2002, 1169–1176.

[5] A. Rozzi, N. Limoni, S. Menegatti, G. Boari, L. Liberti, and R. Passino, “Influence of Na and Ca alkalinity on UASB treatment of olive mill effluents. Part 1. Preliminary results,”*Process Chem*. 23, 1988, 86–90.

[6] L. M. Nieto, G. Hodaifa, S.R. Vives, and J.A. Casares, “Industrial plant for olive mill wastewater from two-phase treatment by chemicals oxidation,” ***J. Environ. Eng.*** 136(11), 2010, 1309-1313.

[7] L.M. Nieto, S.B. Driss, G. Hodaifa, C. Faur, S.R. Vives, J.A. Gimenez, and J. Ochando-Pulido, “Adsorption of iron on crude olive Stones,”***Ind. Crop. Prod***. 32, 2010, 467–471.

[8] B. Bianco, I. D. Michelis, and F. Vegliò, “Fenton treatment of complex industrial wastewater: Optimization of process conditions by surface response method,” ***J. Hazard. Mater.*** 186, 2011, 1733–1738.

[9] Ersoy, I. Tosun, A. Günay, and S. Dikmen, “Turbidity removal from wastewater of natural stone processing by coagulation/flocculation methods,”*Clean*37 (3), 2009, 225-232.

[10] L. Yan, H. Tao, and P.R. “Bangal, Synthesis and flocculation behaviour of cationic cellulose prepared in a NaOH/urea aqueous solution,” *Clean*37 (1), 2009, 39-44.

[11] A.A. Tatsi, A.I. Zouboulis, K.A. Matis, and P. Samara, “Coagulation–flocculation pre-treatment of sanitary landfill leachates,” *Chemosphere* 53, 2003, 737–744.

[12] H.I. Abdel-Shafy, and S.E. Abdel-Basir, “Chemical treatment of industrial wastewater,” Environ. Manage. Health 2(3), 1991, 19–23.

[13] M. Rossini, J. García, and M. Galluzzo, “Optimization of the Coagulation–Flocculation Treatment: Influence of Rapid Mix Parameters,” Water Res. 33, 1999, 1817– 1826.