

# Effect of alkali agents in the pre-treatment of cheese whey wastewater by coagulation-flocculation processes

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## Abstract

The use of aluminium ( $\text{Al}_2(\text{SO}_4)_3$ ) and iron ( $\text{FeSO}_4$ ) salts to treat acid cheese whey wastewater (CWW) requires a previous pH adjustment with alkali agents like hydrated lime and sodium hydroxide. In this work, four different sequences have been tested:  $\text{Al}_2(\text{SO}_4)_3+\text{NaOH}$ ;  $\text{Al}_2(\text{SO}_4)_3+\text{lime}$ ;  $\text{FeSO}_4+\text{NaOH}$  and  $\text{FeSO}_4+\text{lime}$ .

When using  $\text{Al}_2(\text{SO}_4)_3+\text{NaOH}$  the percentage removal of chemical and biological oxygen demands (COD and BOD) obtained were 13% and 21%, respectively. However, application of  $\text{Al}_2(\text{SO}_4)_3+\text{lime}$  demonstrated to be more effective, with COD and BOD eliminations of roughly 36%.

The  $\text{FeSO}_4+\text{lime}$  coagulation process led to COD and BOD removals in the range 43-67%. The clarified supernatant showed an almost complete turbidity removal and a decrease  $\geq 70\%$  of the absorbance measured at 220, 254, 292 and 410 nm.

Sodium hydroxide presents some advantages such as less conductivity of supernatant (-20%) and sludge volume, but the lime alkalizing agent is favoured from the point of view of economics and removal efficacy.

**Keywords:** Cheese whey wastewater; coagulation-flocculation; alkali agents

## I. Introduction

The process of making cheese involves common general procedures to most cheeses and can be summarized by the following basic steps: Milk used in cheese manufacturing is stored at low temperature in stainless steel tanks. This milk is then sent to coagulation by the addition of microbial or vegetable rennet. After a certain time, the fermented milk produces the curds that is cut and converted in the commercial product - cheese and a by-product – Cheese whey (CW). Part of the cheese whey, resulting from hard cheese production is processed to obtain cottage cheeses, called in Portugal (*Requeijão*), Italy (*Ricotta*), Spain (*Requesón*), Greece (*Manouri*), and other names like *curd cheese*, *cottage cheese* and *curd*. Moreover, the production of *Requeijão* still leads to the generation of a second cheese whey or cottage cheese whey, usually called *Sorelho in Portugal* (Pereira et al., 2002).

The washing water of storage tanks and pipelines generates an effluent called Cheese whey wastewater (CWW) that generally contains CW, SCW and washing water.

The presence of lactose in the CWW makes this a singular effluent, because the lactose needs high hydraulic retention time and specific microorganisms for its degradation. The high organic load requires an effluent dilution.

The existence of proteins, mainly casein with an isoelectric point of 4,6 and the need of pH increase for the correct use of the coagulants, makes the proteins to precipitate at high pH. In fact a higher COD removal was achieved with  $\text{FeSO}_4$  at pH 8,5 if compared to the use of  $\text{FeCl}_3$  utilized at the natural pH of CWW, 4,5 (Rivas et al., 2010).

Rivas et al., 2011, obtained the best results in organic matter removal when using lime and NaOH precipitation at the highest pH tested. Almost 50% of COD was removed in the lime and NaOH precipitation. The precipitation considered as a pre-treatment of the CWW makes the supernatant easily biodegradable.

## II. Methodology

**Wastewater.** The CWW studied was collected from a small industry located in the “Serpa Cheese” region of Alentejo, Portugal. Table 1 depicts the main properties of this effluent: low pH and high salinity are the consequence of the type of whey produced. The main parameters of this effluent are COD and BOD values that were found to be 10,65 and 12,5 g/L, respectively (BOD should not be higher than COD, the maximum BOD/COD ratio is 1.0). The ratio BOD/COD suggests that the effluent has a high biodegradability value.

However, when this wastewater was treated by aerobic degradation a HRT of approximately 8 days was required. Thus, the slow biodegradation constitutes the principal limiting factor of the biological processes. Additionally, the effluent also presents high values of chloride and total suspended solids. The latter parameter has a value similar to the one reported by Gavala et al., [1999].

Components like proteins and lactose are present, but in small quantities compared to those obtained by Yang et al. [2003] and Lee et al. [2006], these results are due to the anoxic lagoon conditions. These conditions lead to the conversion of the lactose to lactic acid, lowering the pH and causing the precipitation of casein. This wastewater presents a disagreeable odor of butyric acid that causes discomfort and attracts insects such as flies and mosquitoes. Additionally, the CWW has a significant fat content, with values within the range reported by Kalyuzhnyi et al. [1997], which causes sludge floatation in the anaerobic processes [Perle et al., 1995].

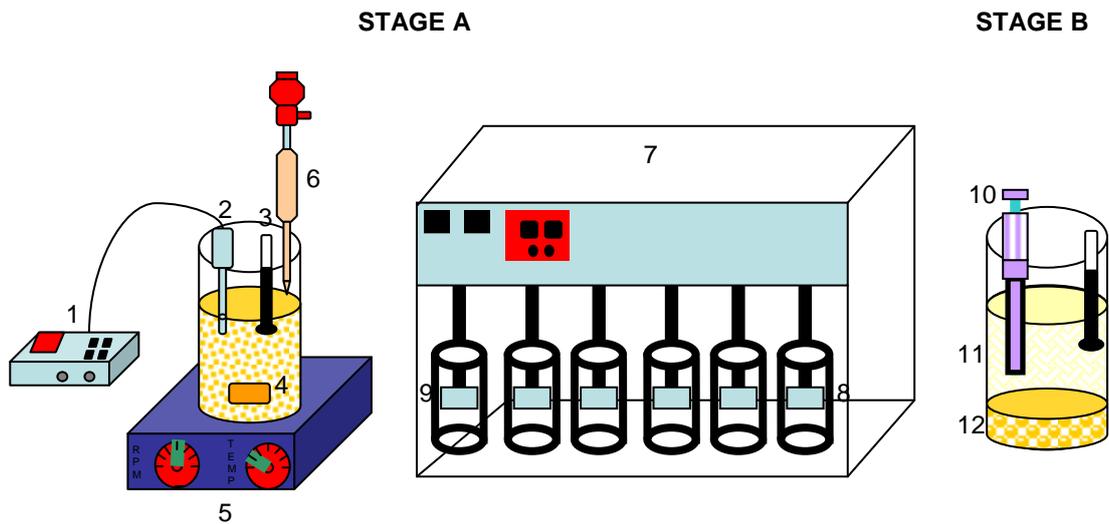
**Table 1. Characterization of CWW from the Production of “Serpa Cheese”<sup>a</sup>.**

Parameter	Units	Interval	Average value
<i>pH</i>	-	4,01-4,55	4,23±0,01
<i>Redox Potential</i>	mV	-436,5-148,6	5,8±169,1
<i>Temperature</i>	° C	10-15	12±1
<i>Conductivity</i>	mS/cm	11,25-13,47	12,39±1,11
<i>COD</i>	mg O <sub>2</sub> /L	8838-25583	1349±4270
<i>BOD<sub>5</sub> pH=7,0</i>	mg O <sub>2</sub> /L	1000-12500	11686±962
<i>BOD<sub>5</sub> at no modified pH</i>	mg O <sub>2</sub> /L	2350-8400	6342±2351
<i>BOD<sub>20</sub> at no modified pH</i>	mg O <sub>2</sub> /L	1200-12400	952±4692
<i>BOD<sub>5</sub>/COD at pH 7,0</i>	-	0,79-1,17	1,05±1,16
<i>BOD<sub>5</sub>/COD</i>	-	0,31-0,41	0,38±0,05
<i>Turbidity</i>	NTU	1331-2004	1557±219
<i>Total solids</i>	mg/L	7016-8348	7910±613
<i>Total suspended solids</i>	mg/L	1628-4780	3317±1269
<i>Total dissolved solids</i>	mg/L	4256-4850	4729±264
<i>Chloride</i>	mg/L	2119-2838	2501±248
<i>Oil and fats</i>	mg/L	1830-3758	2489±711
<i>Kjeldahl nitrogen</i>	mg/L N-Kj	309,9-355,5	323,7±18,4
<i>Ammonium nitrogen</i>	mg/L N-NH <sub>3</sub>	51,9-70,5	62,9±7,3
<i>Phosphorus</i>	mg P/L	6,6-7,2	6,9±0,3
<i>Total Protein</i>	µg/L	938-947	943±6
<i>Lactose</i>	mg/L	178-182	180±3
<i>220 nm<sup>b</sup></i>	cm <sup>-1</sup>	0,609-0,878	0,736±0,105
<i>254 nm<sup>b</sup></i>	cm <sup>-1</sup>	0,324-0,470	0,370±0,045
<i>292 nm<sup>b</sup></i>	cm <sup>-1</sup>	0,248-0,359	0,285±0,035
<i>386 nm<sup>b</sup></i>	cm <sup>-1</sup>	0,156-0,207	0,172±0,016
<i>410 nm<sup>b</sup></i>	cm <sup>-1</sup>	0,142-0,190	0,158±0,016

<sup>a</sup>Number of measurements: 34 for pH, 26 for COD, 16 for Absorbance and turbidity, and 7 for the rest of the parameters. <sup>b</sup> 1:50 dilution

**Analytical Procedures.** pH and redox potential were monitored in a WTW InoLab apparatus. Conductivity and turbidity were quantified in a Jenway 4510 meter and WTW Turb550 turbidimeter, respectively. COD, solids, ammonium and Kjeldahl nitrogen were determined by standards methods [APHA, 1998]. BOD, lactose, proteins and chloride were analyzed by respirometric, Tell [Teles et al., 1978], Lowry and Mohr methods, respectively. Phosphorus was evaluated from colorimetric method by the reaction of orthophosphates with vanadate-molibdate reagent [APHA, 1998] after calcination at 600°C and dry digestion. For oil and fats measurement the gravimetric method after Soxhlet extraction [Sawyer et al., 1994] was used. The absorbance 220 nm (low-molecular-weight compounds), 254 nm (aromatic and unsaturated compounds), 292 nm (aromatic amino acids and aliphatic volatile compounds with a conjugated chain), 386 nm (carbohydrates) and 410 nm (color) [Kasprzyk-Hordern et al., 2006; APHA, 1998; Peuravuori et al., 2002; Pacheco and Peralta-Zamora, 2004; Rivas et al., 2005] were measured in a Ultrospec 2100pro spectrophotometer.

**Precipitation experiments.** Jar-Tests were conducted in 1-L glass recipients by using a wastewater volume of 800 mL. The pH meter was immersed in the samples and the alkali agent (NaOH or Ca(OH)<sub>2</sub>) was added to raw CWW under rapid agitation until the desired pH. The coagulant dose was added under initial fast agitation (150 rpm) for 2 min and further slow agitation (20 rpm) for 20 min. After sludge sedimentation, the samples were collected and analyzed to determine the main contaminant indicators.



**Figure 1. Schematic diagram of the experimental installation. Stage A-pH correction:** (1) pH meter, (2) pH electrode, (3) glass thermometer, (4) magnetic stirrer, (5) stirring plate, (6) pH corrector ( $H_2SO_4$ ), (7) jar test, (8) agitation system, (9) glass. **Stage B-Sedimentation:** (10) Sampling, (11) clarified wastewater, (12) white precipitate.

### III. Results and Discussion

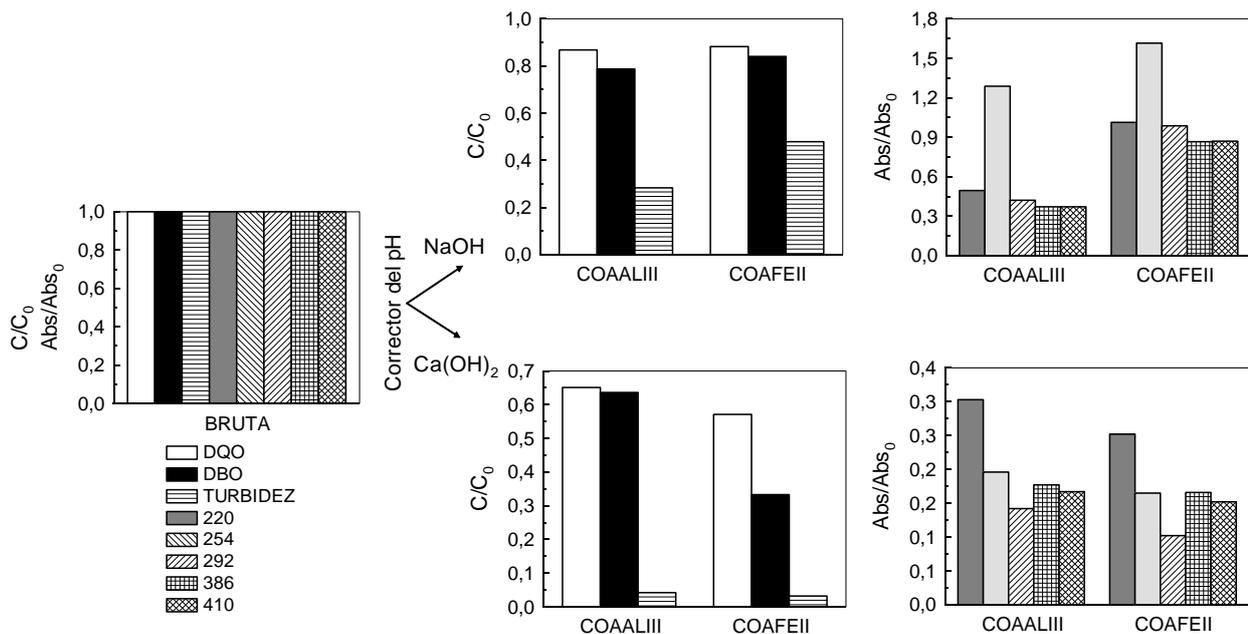
#### III.1. Influence of alkali agents ( $Ca(OH)_2$ and $NaOH$ ) in Organic matter removal by coagulation - flocculation of CWW

The use of  $Al_2(SO_4)_3$  or  $FeSO_4$  in the raw CWW coagulation requires a pH increase to 7 or 8.5, respectively. In this work, the pH was corrected with two different alkali agents:  $NaOH$  or  $Ca(OH)_2$  and their influence in organic matter removal were studied by the parameters: COD,  $BOD_5$ , turbidity, and specific absorbances.

The results obtained are summarized in Figure 2. As seen, the organic matter removal is higher when the alkali agent applied was  $Ca(OH)_2$ . Use of  $Al_2(SO_4)_3$  led to COD and  $BOD_5$  abatement values of 13% and 21%, respectively, when the alkali agent was  $NaOH$  and 35 and 36 % when adding  $Ca(OH)_2$ .

When  $FeSO_4$  was considered, removals of COD and  $BOD_5$  of 12 and 16 %, respectively were experienced after  $NaOH$  pH adjustment. Use of  $Ca(OH)_2$  as pH corrector involved COD and  $BOD_5$  removals to values of 43% and 67% respectively.

The removal of turbidity and specific absorbance was also higher when using  $Ca(OH)_2$  [70-97%].

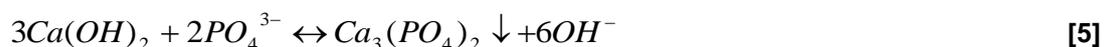
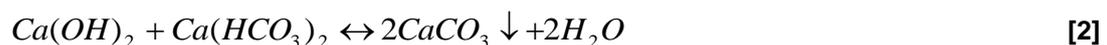


**Figure 2.** Influence of the Alkali agents in organic matter removal (COD and  $DBO_5$ ), turbidity and characteristic absorbance. Experimental conditions: NaOH:  $T=21,2\text{ }^\circ\text{C}$ ;  $pH_0=4,50$ ; redox potential  $=-583,1$ ;  $COD_0=10400\text{ mg/L}$ ;  $BOD_0=9400\text{ mg/L}$ ;  $BOD/COD=0,90$ ; Turbidity= $1790,5\text{ NTU}$ ; Abs 2200 (dilution 1:50)= $0,771$ ; Abs 2540 (dilution 1:50)= $0,470$ ; Abs 2920 (dilution 1:50)= $0,359$ ; Abs 3860 (dilution 1:50)= $0,202$ ; Abs 3850 (dilution 1:50)= $0,202$ ; Abs 4100 (dilution 1:50)= $0,185$ ; Conductivity  $=12,44\text{ mS/cm}$ .  $Ca(OH)_2$ :  $T=12,0\text{ }^\circ\text{C}$ ;  $pH_0=4,25$ ; redox potential  $=86,0$ ;  $COD_0=13900\text{ mg/L}$ ;  $BOD_0=11000\text{ mg/L}$ ;  $BOD_5/COD=0,79$ ; Turbidity= $1714,7\text{ NTU}$ ; Abs 2200 (dilution 1:50)= $0,642$ ; Abs 2540 (dilution 1:50)= $0,368$ ; Abs 2920 (dilution 1:50)= $0,280$ ; Abs 3860 (dilution 1:50)= $0,179$ ; Abs 3850 (dilution 1:50)= $0,181$ ; Abs 4100 (dilution 1:50)= $0,164$ ; Conductivity $_0=13,47\text{ mS/cm}$ .

These differences observed in the organic matter removal can be attributed to additional reactions between alkali agents and CWW.

The addition of  $Ca(OH)_2$  in the presence of enough alkalinity ( bicarbonates), hardness and phosphates can lead to the following reactions [Eckenfelder, 2000; Semerjian y Ayoub 2003; Renou *et al.*, 2008]:

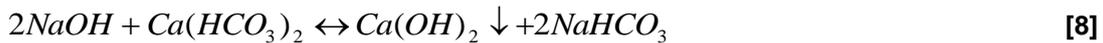
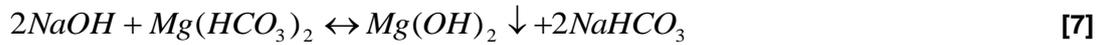
With addition of  $Ca(OH)_2$ , in the presence of enough alkalinity ( bicarbonates), hardness and phosphates can give rise to the following reactions [Eckenfelder, 2000; Semerjian and Ayoub, 2003; Renou *et al.*, 2008]:



Addition of  $Ca(OH)_2$  allows for the precipitation of calcium carbonate (reaction 1-4), carbonate and magnesium hydroxides (reaction 3 and 4) and phosphates (reaction 5 and 6), trapping and dragging the suspended and colloidal particles (sweep coagulation) increasing the effectiveness of organic matter

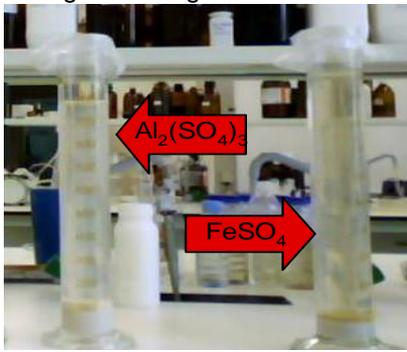
elimination, turbidity and specific absorbances. The  $\text{Ca(OH)}_2$  acts like *weighting agent* increasing the particles density. This effect is more effective in the coagulation with  $\text{FeSO}_4$ .  $\text{Ca(OH)}_2$  is effective in the precipitation of phosphates, trace of metals, microorganisms, COD, BOD, SS, total phosphorus, temporal hardness, humic and fulvic acids [Semerjian y Ayoub, 2003; Renou et al., 2008].

When NaOH is added, the precipitation reaction that can occur is the formation of hydroxide of magnesium and calcium (reactions 7 and 8, Semerjian y Ayoub, 2003). In this case, smaller likely formation of precipitates leads to low drag and fixation of suspended and colloidal particles and consequently, the lowest removal.



Semerjian and Ayoub [2003] refer that the algal and phosphates elimination is lower when NaOH is utilized instead of  $\text{Ca(OH)}_2$ .

During the coagulation with  $\text{FeSO}_4$  and  $\text{Al}_2(\text{SO}_4)_3$ , using  $\text{Ca(OH)}_2$  as pH corrector, the water suffers a discoloration from greenish white to transparent and presents low turbidity, solids and fats.



This aspect change reflects the changes on physico-chemical characteristics of the supernatant with the formation of a white precipitate for  $\text{Al}_2(\text{SO}_4)_3$  sludge and a white- yellow precipitate for  $\text{FeSO}_4$  sludge.

The supernatant from coagulation with  $\text{FeSO}_4$ , utilizing NaOH as pH corrector substance, appears more turbid and the precipitate presents a greenish color. This physical characteristic could mean different reactions, other than with  $\text{Ca(OH)}_2$ , probably due to the formation of precipitates of iron hydroxides II.

### III.2. Biodegradability

The study of the biodegradability of supernatants is summarized in Figure 3.

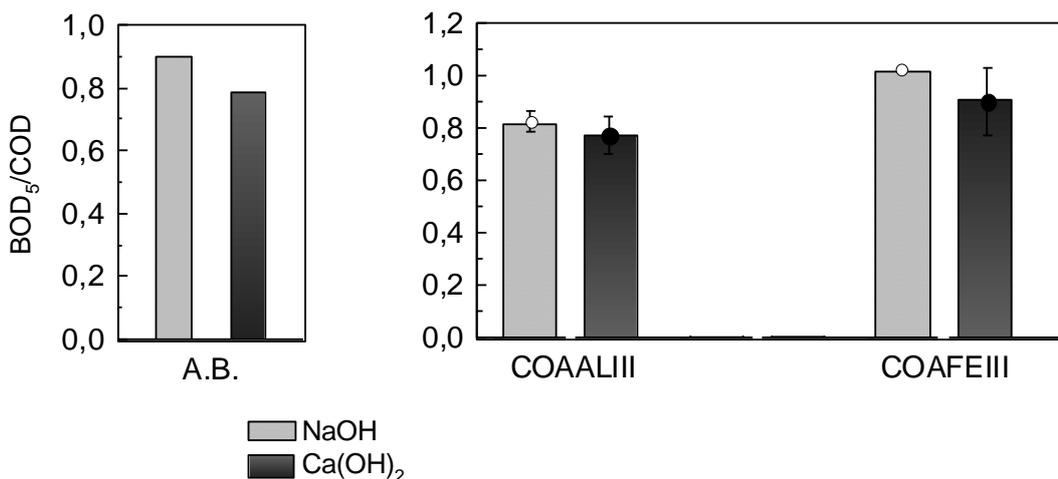
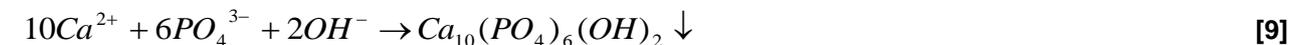


Figure 3. Influence of the alkali agents in the biodegradability of supernatant obtained by coagulation - flocculation. Experimental conditions: COAALIII: 1000 mg/L of  $\text{Al}_2(\text{SO}_4)_3$  at  $\text{pH}=7,00$ ; COAFEII: 250 mg/L of  $\text{FeSO}_4$  at  $\text{pH}=8,50$ ; COAFEIII: 250 mg/L of  $\text{FeCl}_3$  at  $\text{pH}=\text{natural}$ .

As observed, the pH correction with NaOH produces supernatants with high biodegradability index ( $\text{BOD}_5/\text{COD}$ ). The supernatants obtained with  $\text{Ca(OH)}_2$  are more clarified, with less turbidity and organic

matter, but with smaller biodegradability. This fact is likely due to the possible formation of insoluble species (reactions 1-6), that precipitate biodegradable organic matter, total phosphorus, proteins and Kjeldahl nitrogen. The nutrients precipitation leads to a supernatant with low nutrients and biodegradable matter available for the microorganisms..

The phosphorus removal in coagulation - flocculation processes in the presence of  $\text{Ca(OH)}_2$ , can be attributed to the following reactions: [Ramalho, 1996; Eckenfelder, 2000; Metcalf y Eddy, 2003]:



### III.3. Conductivity, sludge volume and consumption of alkali agents

Table 2 summarizes the results obtained for supernatants conductivity; the sludge volume produced and for the mass of alkali needed to change pH to optimum value for coagulation.

Table 2. Influence of the alkali agents in the conductivity, sludge volume and reagent consumption

Parameter	Units	$\text{FeSO}_4$		$\text{Al}_2(\text{SO}_4)_3$	
		NaOH	$\text{Ca(OH)}_2$	NaOH	$\text{Ca(OH)}_2$
Conductivity	(mS/cm)	13,55±0,05	16,94±0,24	13,94±0,36	17,14±0,21
Sludge volume	(mL/L)	65±7,57	87±7,64	113±23,68	130±0,00
Mass of alkali agent	(g/L)	1,82	4,10±0,26	1,73	3,07±0,06

The analysis of the table shows that the use of the alkali NaOH leads to supernatants with low conductivity. This fact is due to the need for the use of low mass to change the pH. This low mass need can be attributed to the fact that the  $\text{Ca(OH)}_2$  is obtained from the lime and the lime isn't a pure reactant. The  $\text{FeSO}_4$  produces lower sludge volume, independently of the substance utilized, but the use of  $\text{Ca(OH)}_2$  allows higher volume of sludge than NaOH, probably due to a greater removal of organic matter.

## IV. Conclusions

This work presents the study of the effect of alkali agents in the coagulation – flocculation process, particular in the COD, BOD, turbidity, conductivity and sludge volume. As the raw effluent presents an acidic pH, the use of coagulation - flocculation step necessarily needs a pH adjustment to achieve maximum organic removal. It can be concluded that the alkali agents influence the organic load removal and the supernatant's biodegradability. The amount of sludge is also influenced by the alkali agent and is higher for the maximum removal organic load, with  $\text{FeSO}_4$ +lime. On the other hand, these processes are favoured at high pH, because at this pH the proteins are negatively charged favouring coagulation.

## Literature Cited

- APHA (1998). *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association, 20<sup>th</sup> Ed. Washington DC, USA.
- Eckenfelder, W.W. (2000). *Industrial Water Pollution Control*. 3<sup>a</sup> Edition, McGraw-Hill, New York, United States.
- Gavala, H.N.; Kopsinis, H.; Skiadas, I.V.; Stamatelatou, K. and Lyberatos, G. (1999). Treatment of Dairy Wastewater Using an Upflow Anaerobic Sludge Blanket Reactor. *J Agr Eng Res*, 73 (1), 59-63.
- Kalyuzhnyi, S.V.; Martinez, E.P. and Martinez J.R. (1997). Anaerobic Treatment of High-Strength Cheese-Whey Wastewater in Laboratory and Pilot UASB - Reactors. *Bioresource Technol*, 60 (1), 59-65.
- Kasprzyk-Hordern, B; Raczky-Stanislawiak, U.; Swietlik, J. And Nawrocki, J. (2006). Catalytic Ozonation of Natural Organic Matter on Alumina. *Appl Catal B-Environ*, 62 (3-4), 345-358.
- Lee, C.; Kim, J. and Hwang, S. (2006). Optimization of Adenosine 5'-triphosphate Extraction for the Measurement of Acidogenic Biomass Utilizing Whey Wastewater. *Biodegradation*, 17 (4), 347-355.
- Metcalf and Eddy (2003). *Wastewater Engineering, Treatment and Reuse*. 4<sup>a</sup> Edition, McGraw-Hill, New York, United States.
- Pacheco, J.R. and Peralta - Zamora, P.G. (2004). Integração de Processos Físico-Químicos e Oxidativos Avançados para Remediação de Percolado de Aterro Sanitário (Chorume). *Eng Sanit Ambient-SciELO Brazil* 9 (4), 306-311.
- Pereira, C.D.; O. Diaz and A. Cobos (2002). Valorization of by-products from ovine cheese manufacture: clarification by thermocalcic precipitation/microfiltration before ultrafiltration. *International Dairy Journal* 12, 773-783.
- Perle, M.; Kimchie, S.H. and Shelef, G. (1995). Some Biochemical Aspects of the Anaerobic Degradation of Dairy Wastewater. *Water Research*, 29 (6), 1549-1554.
- Peuravuori, J.; Koivikko, R. and Pihlaja, K. (2002). Characterization, Differentiation and Classification of Aquatic Humic Matter Separated With Different Sorbents: Synchronous Scanning Fluorescence Spectroscopy. *Water Res*, 36 (18), 4552-4562.
- Ramalho, R.S. (1996). *Tratamiento de Aguas Residuales*. Edición revisada, Editorial Reverté, S.A., Barcelona, España.

- Renou, S.; Poulain, S.; Givaudan, J.G. and Moulin, P. (2008). Treatment Process Adapted to stabilized Leachates: Lime Precipitation–Prefiltration–Reverse Osmosis. *Journal of Membrane Science*, 313, 9–22.
- Rivas, F.J.; Beltrán F.; Carvalho, F.; Gimeno, O. and Frades, J. (2005). Study of Different Integrated Physical-Chemical + Adsorption Processes for Landfill Leachate Remediation. *Ind Eng Chem Res*, 44 (8), 2871-2878.
- Rivas, J.; Prazeres, A.R. and Carvalho, F. (2011). Aerobic Biodegradation of Pre-Coagulated Cheese Whey Wastewater. *J Agr Food Chem*, 59 (6), 2511-2517.
- Rivas, J.; Prazeres A.R.; Carvalho, F. and Beltrán, F. (2010). Treatment of Cheese Whey Wastewater: Combined Coagulation-Flocculation and Aerobic Biodegradation. *J Agr Food Chem*, 58 (13), 7871–7877.
- Semerjian, I. and Ayoub, G.M. (2003). High-pH–Magnesium Coagulation–Flocculation in Wastewater Treatment. *Advances in Environmental Research*, 7, 389-403.
- Teles, F.F.; young, C.K. and Stull, J.W. (1978). A Method for Rapid Determination of Lactose. *J Dairy Sci*, 61 (4), 506-508.
- Yang, K.; Yu, Y. and Hwang, S. (2003). Selective Optimization in Thermophilic Acidogenesis of Cheese-Whey Wastewater to Acetic and butyric Acids: Partial Acidification and Methanation”. *Water Res*, 37 (10), 2467-247

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