CHEESE WHEY WASTEWATER TREATMENT BY ACIDIC PRECIPITATION

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Abstract

Cheese whey wastewater (CWW) is characterized by a relative high chemical and biological oxygen demand values (COD and BOD), accordingly appropriate treatments are required. The precipitation of CWW in acidic conditions has been investigated. Decreasing the initial pH of CWW to values in the range 1-3 results in the formation of a white precipitate. This precipitate presents flocculent sedimentation involving the subsequent partial removal of organic load. Removal efficiencies of 21% of COD and 41% of BOD, were obtained in optimal conditions (pH=1,0). The supernatant obtained presents a high redox potential value and biodegradability (BOD/COD≈0,89±0,10). Moreover, the acidic precipitation allows an average phosphorus depletion≈18% and similar results were obtained when the kjeldahl nitrogen was monitored. The supernatant showed an average of 12% in turbidity removal and a decrease of 33-54% in the absorbance measured at 220, 254, 292 and 410 nm.

Keywords: *Cheese whey wastewater; acidic precipitation; organic matter removal; biodegradability*

I. Introduction

The principal key parameters of the dairy effluents show a relative high organic load, monitored by BOD and COD in the range of 0,2 to 100 g/L with index of biodegradability (BOD_5/COD) typically in the range 0,4-0,8. This organic matter is due to the presence of the main carbohydrates and proteins of the milk, like lactose and casein, respectively. The milk processing in the cheese production leads to the generation of a large volume of cheese whey – CW. The daily discharge of whey resulting from the cheese manufacture, in Portugal, was estimated to be around 1 million of liters. The washing water of pipelines and storage tanks generates an effluent called Cheese whey wastewater (CWW), that generally contains CW (and/or SCW - second cheese whey) and washing water in the proportion 1:5.

The CWW management has concentrated in the biological and/or physicochemical treatment and needs technologies capable to remove more than 95% of organic matter for the discharge in the environment. CWW has a moderate to high content of easily biodegradable organic matter; consequently the conventional treatments of CWW are based on anaerobic and aerobic digestions. However, the majority of studies have been carried out in anaerobic conditions using UASB reactors to treat raw CWW [Gutiérrez et al., 1991; Kalyuzhnyi et al., 1997; Gavala et al., 1999] and diluted CWW [Gavala et al., 1999] at neutral pH and room temperature or mesophlilic conditions. In these situations, the COD removal can achieve values between 81-99% for raw CWW and 85-98% for diluted CWW. Additionally, some studies were carried out in aerobic conditions to treat raw CWW, mainly by activated sludge processes [Fang, 1991; Martins and Quinta, 2010; Rivas et al., 2010; Rivas et al., 2011]. Elimination of the principal contaminant indicators in the range 95-99% have been reported. Regarding the physicochemical treatments, only a few studies were found dealing with raw CWW by coagulation-flocculation [Rivas et al., 2010] and precipitation [Rivas et al., 2011] or pretreated CWW by ozonation [Martins and Quinta-Ferreira, 2010] and Fenton processes [Martins et al., 2010].

The present biological treatment technologies allow for the organic matter removal exceeding 80% of the initial load, however, these technologies normally require a high Hydraulic Retention Time (HRT). Moreover, it is notable that, in most of cases, a final effluent that cannot be discharged into the environment is generated. The aforementioned effluent normally exceeds the legal limits imposed by European Environmental Legislations, not only by considering the organic matter load (COD and BOD), but also because of the nutrients content. This drawback is of special concern in sensitive areas, where the N and P can cause the eutrophication of surface waters. Additionally, traditional cheese factories are of small to medium scale having low economic and technical capacity. For these reasons, innovative treatments are unavoidable and imperative. Hence, this work is focused on the investigation of a pre-treatment by acidic precipitation applied to raw CWW under different conditions.

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. 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".

Parameter	Units	Interval	Average value	Standard deviation
pH	-	4,23-4,24	4,24	**0,01**
Redox Potential	mV	-	44,2	**-**
Temperature	º C	10-15	12	**1**
Conductivity	mS/cm	11,25-13,47	12,39	**1,11**
COD	mg O_2/L	9463-11838	10650	**1679**
BOD_5 pH=7,0	mg O_2/L	-	12500	**-**
BOD_5/COD	-	-	1,17	-
Turbidity	NTU	-	1345,2	-
Total solids (TS)	mg/L	-	8283	**-**
Total suspended solids (TSS)	mg/L	-	4780	**-**
Total dissolved solids (TDS)	mg/L	-	4847	**-**
Chloride	mg/L	2572-2838	2690	**135**
Oil and fats	mg/L	1830-2162	1987	**167**
Kjeldahl nitrogen	mg/L N-Kj	309,9-320,9	314,5	**5,8**
Ammonium nitrogen	mg/L N-NH_3	68,5-70,5	69,4	**1,1**
Phosphorus	mg P/L	6,8-7,2	7,0	**0,3**
Total Protein	μg/L	938-947	943	**6**
Lactose	mg/L	178-182	180	**3**
220 nm[a]	cm^{-1}	-	0,664	-
254 nm[a]	cm^{-1}	-	0,412	**-**
292 nm[a]	cm^{-1}	-	0,322	**-**
386 nm[a]	cm^{-1}	-	0,185	**-**
410 nm[a]	cm^{-1}	-	0,170	-

[a]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 600ºC and dry digestion. For oil and fats measurement the gravimetric method after Sohxlet 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 an 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 acid precipitant (H_2SO_4) was added to raw CWW under rapid agitation until the desired pH. When pH of precipitation was obtained the agitation was stopped. After sludge sedimentation, the samples were collected and analyzed to determine the main contaminant indicators.

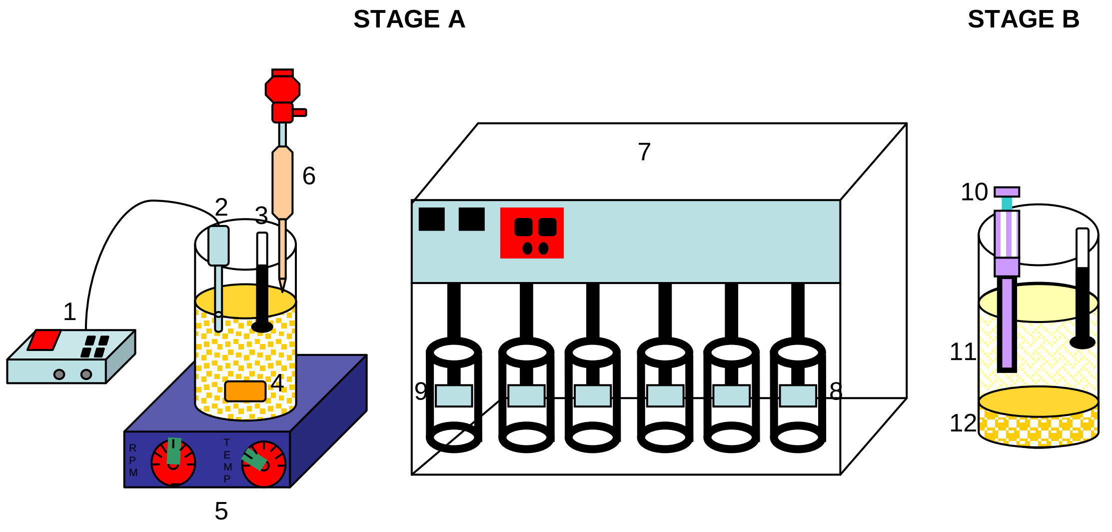

Figure 1. *Schematic diagram of the experimental installation*. Stage A-pH correction: (1) pH meter, (2) pH electrode, (3) glass thermometer, (4) magnetic stirrer, (5) stirring plate, (6) pH corrector (H_2SO_4), (7) jar test, (8) agitation system, (9) glass. **Stage B-Sedimentation**: (10) Sampling,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

III. Results and Discussion

Precipitation by acidification with sulfuric acid: optimal conditions.

Sulfuric acid addition to raw CWW allows for the decrease of the initial pH=4,24 to values in the range 1-3 leading to the formation of agglomerated particles that after a short time originate a white precipitate. This precipitate presents flocculent sedimentation. The precipitate formation involves the partial organic matter load removal monitored by COD and BOD. Turbidity, total suspended solids, nitrogen compounds, etc. are also reduced to some extent.

A first series of precipitation experiments was conducted to assess the best pH operating conditions. Figure 2 illustrates the main results obtained in terms of COD, BOD, turbidity, biodegradability, TSS, pH, etc. at different pH´s.

As inferred from this figure, the pH of the supernatant was close to the pH used in the precipitation while the potential redox increases with acidity, approximately 100 mV per unit of pH increased. Remaining supernatant COD is linearly related to precipitation pH (r^2=0,86). It was found that the COD elimination increases with acidic conditions, thus at pH=1,0 the COD removal was maximum with a value of approximately 25%. Additionally, this supernatant presents the highest value of biodegradability (BOD/COD=0,99). BOD removals in the proximity of 40% can be achieved at pH=1,0. Absorbance reductions between 23-47% for optimum pH are also experienced.

A value of pH=2,0 allows a significant TSS removal of 70,5%, however the supernatant presents a low biodegradability. As a consequence, this pH value is not appropriate as a pretreatment for biological processes.

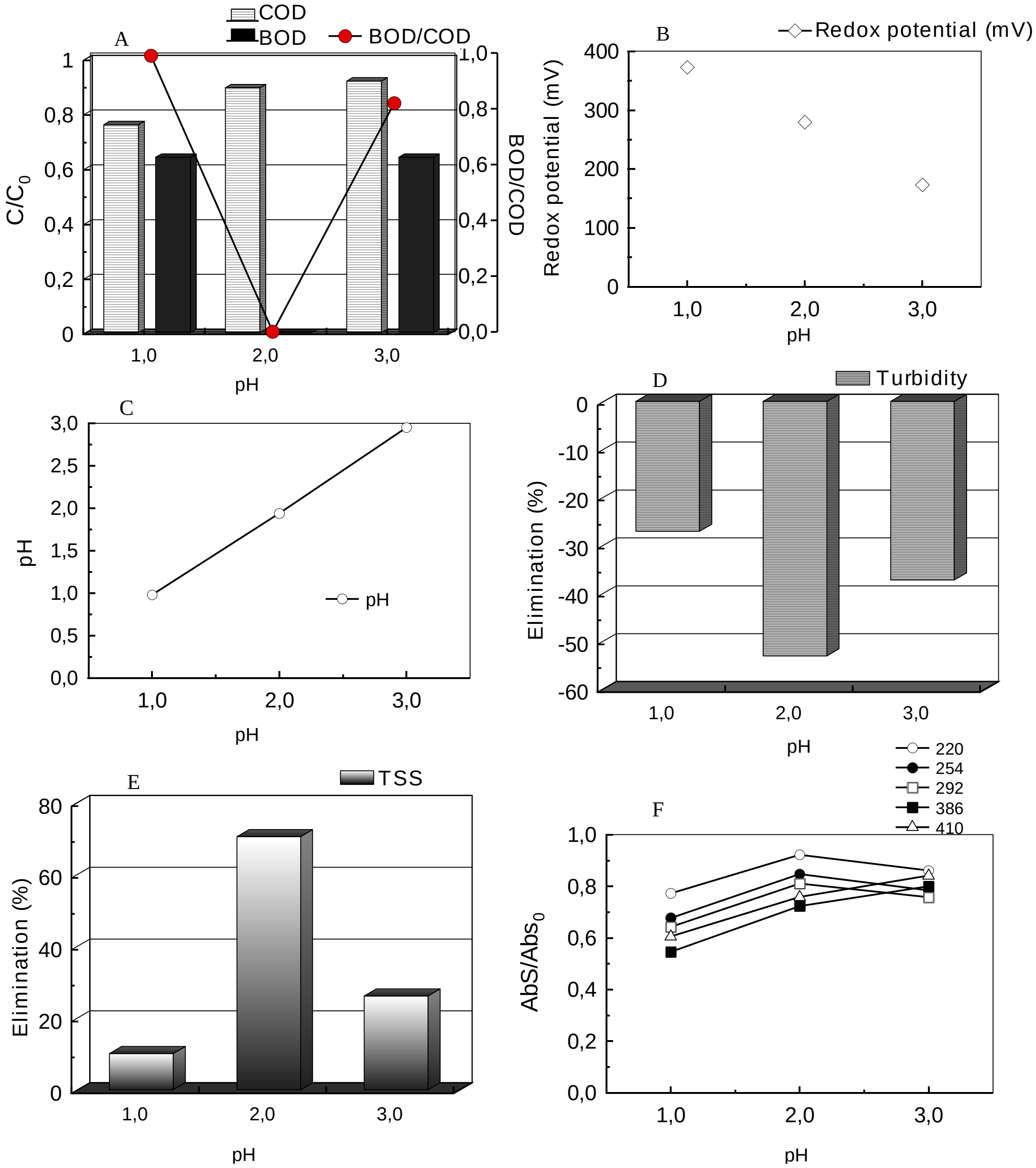

Figure 2. Acidic precipitation of raw CWW at different pH.

Characterization of the supernatant after acid precipitation

The characterization of the supernatant obtained in replication experiments carried out with the best operating conditions is presented in Table 2. As observed, the supernatant presents low pH and a high value of conductivity.

Acid precipitation applied to raw CWW permits COD and BOD average eliminations around 21 and 41%, respectively. Coagulation-flocculation with $FeSO_4$ [Rivas et al., 2010] is more effective in the supernatant clarification. Thus, turbidity elimination can have values in the proximity of 97%, compared to 12% for turbidity reduction and 21% of TSS reduction found in this work. However, the biodegradability of the supernatant obtained by acid precipitation is about 2 times higher compared to the results obtained from coagulation-flocculation with $FeSO_4$. This effect can be caused by the high depletion of nutrients in the $FeSO_4$ process, like phosphorus (89%) and nitrogen compounds (43%). Thus, the lower elimination of nutrients, about 18%, found in the acid precipitation can constitute an advantage for the application of a biological post-treatment.

The elimination of total proteins was 17% and reduction of absorbance measurements were found in the range 33-54%.

Table 2. Characterization of supernatant after acid precipitation of raw CWW.

Parameter	Units	Interval	Average value	Standard deviation
pH	-	0,98-1,16	1,07	0,13
Redox potential	mV	452,9-458,7	455,5	2,9
Conductivity	mS/cm	43,30-44,10	43,70	0,57
COD	mg O_2/L	7776-9400	8421	862
BOD_5 pH=7,0	mg O_2/L	6900-8000	7433	551
BOD_5/COD	-	0,79-0,99	0,89	0,10
Turbidity	NTU	648,8-1709,9	1179,4	750,3
TS	mg/L	12200-12790	12495	417
TSS	mg/L	3240-4300	3770	750
TDS	mg/L	8910-9530	9220	438
Oil and fats	mg/L	2240-2967	2604	514
Total nitrogen	mg/L N-Kj	254,5-262,8	258,6783	5,9
Ammonium nitrogen	mg/L N-NH_3	63,6-63,6	63,6321	0,0
Phosphorus	mg P/L	5,7-5,9	5,833	0,1
Total Protein	μg/L	769-796	783	19
Lactose	mg/L	178-191	185	9
220 nm[a]	cm^{-1}	0,375-0,513	0,444	0,098
254 nm[a]	cm^{-1}	0,168-0,279	0,224	0,078
292 nm[a]	cm^{-1}	0,106-0,207	0,157	0,071
386 nm[a]	cm^{-1}	0,069-0,101	0,085	0,023
385 nm[a]	cm^{-1}	0,069-0,113	0,091	0,031
410 nm[a]	cm^{-1}	0,062-0,103	0,083	0,029

[a] 1:50 dilution

IV. Conclusions

This work presents the study of the acid precipitation, as a pre-treatment of cheese whey wastewater, based on the organic matter and nutrients removal.

The principal conclusions can be summarized below:

- in the range of pH=1-3, the optimal conditions are achieved when using the lowest pH. Organic removal about 21% and 41% for COD and BOD are experienced, respectively;
- 12% for turbidity reduction and 21% for TSS removal were obtained;
- elimination of nutrients (P and N-Kj), about 18% was also noticed.
- the COD, pH and redox potential of supernatant obtained have a linear relationship with precipitation pH;
- the supernatant is not suitable for direct discharge and a post-treatment is necessary;
- the high biodegradability of the supernatant permits a further biological treatment;
- low nutrient elimination compared to coagulation and basic precipitation constitutes an advantage, when biological post-treatment is used.

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Acknowledgements

The authors thank the economic support received from the Research Group TRATAGUAS (Spain) and Fundação para a Ciência e a Tecnologia, Ministério da Ciência, Tecnologia e Ensino Superior (Portugal), under the QREN - POPH.

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