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Reduction of Total Phenols, Total Phosphorus and Turbidity by Uncatalytic Oxidation Processes in Cheese Whey Wastewater †

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Abstract: This study reports the first time that cheese whey wastewater has been treated by the hydrogen peroxide oxidation alone (uncatalytic reaction). This oxidation type was capable of eliminating the total phosphorus content in about 46–53%, regardless of the dose applied (1–7 g L^{-1}). For total phenols contents, the oxidation system was capable of reducing around 40% under the lowest concentration investigated (1 g L^{-1}). Similar results were obtained for calcium content with a reduction of 55%. Turbidity was reduced in about 90% when hydrogen peroxide was applied with concentrations of 2, 3 and 7 g L^{-1}. Characteristic absorbances were reduced in the range of 12–83% depending on the operating conditions. Chemical oxygen demand (COD) was recalcitrant to hydrogen peroxide oxidation alone (uncatalytic reaction), needing a post-treatment.

Keywords: cheese effluents; chemical oxidation; uncatalytic reaction; hydrogen peroxide; treated effluent

1. Introduction

Cheese whey is simultaneously a strong wastewater for the environment and public health and an interesting resource for the production of value added products [1]. The properties of cheese whey wastewater differ significantly, depending on type of milk processed, system type, amount of cheese whey produced and valorized, quality and quantity of cleaning water used. Cheese whey wastewater is principally constituted by fractions of milk, cheese whey and washing water with alkaline and acidic compounds coming from the washing of equipment and tanks.

Cheese whey wastewater presents high content of organic matter evaluated by chemical and biochemical oxygen demand (COD and BOD) due to the presence of proteins, fats and lactose [2]. Consequently, this wastewater is responsible for high consumption of oxygen in receptor mediums. The levels of nitrogen and phosphorus are related with a high risk of eutrophication in receiving waters [2]. Additionally, cheese whey wastewater exhibits high salinity and total suspended solids content and biodegradability, and low pH and alkalinity, needing an adequate management. The

BOD/COD ratio presents values above 0.5, being an important substrate for anaerobic and aerobic degradation [2].

Several technologies have been investigated to deal with this complex problem, principally biological processes [3–8]. Despite the high removal of organic matter [9,10], biological processes present complications in the stability of the reactors. In this sense, cheese effluents have a relation of carbon, nitrogen and phosphorus of C/N/P ≈ 200/3.5/1, being deficient in nitrogen for aerobic and anaerobic technologies [2]. On the other hand, biological processes need a high hydraulic retention time and treated effluents present organic matter above the discharge limit. Thus, some physicochemical processes have emerged to address the problems of biological processes.

Coagulation-flocculation with $FeSO_4$, $FeCl_3$ and $Al_2(SO_4)_3$ [11,12], alkaline and acid precipitation with NaOH, $Ca(OH)_2$ and H_2SO_4 [12–16] and oxidation processes with O_3, O_3+H_2O_2, O_3+N-150 (Fe_2O_3-MnOx), O_3+Mn–Ce–O (70/30) [17] and Fenton [18] have been applied. Martins and Quinta-Ferreira [17] and Martins et al. [18] reported the reduction of organic matter by oxidation processes in pretreated cheese whey wastewater. However, no study reports the reduction of total phenols, total phosphorus and turbidity by oxidation processes in raw cheese whey wastewater. Furthermore, no study mentioned the treatment of cheese wastewater using hydrogen peroxide alone (uncatalytic reaction). Thus, in this work, cheese whey wastewater has been treated by oxidation process with hydrogen peroxide alone using different concentrations (1–7 g L^{-1}). The effect of the oxidation process under different concentrations of H_2O_2 on pH, conductivity, characteristic absorbances, calcic and magnesium hardness, alkalinity, COD, total phosphorus, turbidity and total phenols was investigated.

2. Materials and Methods

2.1. Reagents

Hydrogen peroxide 100 volumes (>30% *w*/*v*, M = 34.0 g mol^{-1}) was obtained from Fisher Chemical. Chemical reagents were of analytical grade.

2.2. Cheese Whey Wastewater Collection

Cheese wastewater was coming from an enterprise located in the Alentejo region, Portugal, being collected in a tank. The enterprise has several types of cheeses (sheep and goat cheeses). Polyethylene terephthalate (PET) containers at −20 °C and 4 °C were used to store the raw wastewater before characterization and treatment.

2.3. Methods

pH was measured using a meter Consort C 861 (Consort nv, Bruxelles, Belgique). Temperature and conductivity were monitored in a VWR CO 3100 H apparatus using an electrode VWR CO 11.

Characteristic absorbances were evaluated, after appropriate dilution, in the ultraviolet and visible region using a Thermo Scientific Helios α spectrophotometer (Thermo Scientific, Dreieich, Germany). In the ultraviolet region, absorbances at wavelengths of 220 and 254 nm were measured, while in the visible region, absorbances at wavelengths of 410 and 600 were evaluated. The absorbances at 220, 254, 410 and 600 nm indicate the presence of low molecular weight compounds (simple molecules) formed from complex molecules (humic acids); high molecular weight organic compounds with high degree of aromaticity, high number of double and triple bonds, and phenolic groups; color indicator and optical density of the microorganisms cultures, respectively, [19–25]. Specific absorbance was calculated multiplying the absorbance and dilution used according to Standard Methods [19].

Turbidity was obtained in a WTW Turb550 turbidimeter (WTW, Weilheim, Germany), comparing white light transmitted by the samples and formazine standard suspensions [19,26,27]. COD was evaluated by colorimetric method after a digestion step (150 ± 2 °C for 2 h) in a digester Techne Dri-block DB 200/3 (ERT Lda, Corroios, Portugal) [19,26].

Total phosphorus content was monitored after calcination at 600 °C during 2 h and digestion step with HCl 6 N solution using a heating/stirring plate. The digested samples were filtered using filters WhatmanTM 1001. Total phosphorus was obtained through a colorimetric method by measuring the absorbance at 470 nm after the reaction of orthophosphates with vanadate-molybdate reagent [19]. Total hardness was evaluated by volumetric complexation method and eriochrome black T indicator, while calcium hardness was monitored using the presence of calcon indicator [19]. Magnesium hardness was calculated by difference between total hardness and calcium hardness.

Volumetric method using a solution of known concentration of hydrochloric acid and phenolphthalein indicator and indicator of methyl orange was applied to determine phenolphthalein alkalinity and methyl orange alkalinity. The sum of alkalinity to phenolphthalein and alkalinity to methyl orange corresponds to the total alkalinity.

The spectrophotometric method using the Folin-Ciocalteu phenol reagent was applied to evaluate the total phenols content [28].

2.4. Experimental Procedure

Experiments were developed using 250 mL of raw wastewater. In chemical oxidation, the oxidant (H_2O_2) was added to raw wastewater, which was in agitation of 1200–1400 rpm, to reach concentrations of 1, 2, 3, 4, 5, 6, 7 g L^{-1}. The samples remained with the oxidant under stirring during 24 h at 1200–1400 rpm. Then, stirring was gradually decreasing (700–800 rmp for 1 min followed by 300–400 rpm for 1 min) and particle agglomerates, suspensions and foams sedimented during 24 h. Samples were allowed to stand for 72 h before analysis.

3. Results and Discussion

3.1. Cheese Whey Wastewater Characterization

Cheese wastewater characterization is presented in Table 1.

Table 1. Physicochemical properties of cheese whey wastewater.

Parameter	Units	Interval
pH	Sorensen scale	4.162–4.675
Conductivity	dS m^{-1}	4.86–5.54
Absorbance at 220 nm	(dilution 1:25)	0.599–0.700
Absorbance at 254 nm	(dilution 1:25)	0.157–0.196
Absorbance at 410 nm	(dilution 1:25)	0.083–0.101
Absorbance at 600 nm	(dilution 1:25)	0.053–0.071
Total alkalinity	mg $CaCO_3$ L^{-1}	1155.4–1708.5
Bicarbonates	mg $CaCO_3$ L^{-1}	1155.4–1708.5
Total Hardness	mg $CaCO_3$ L^{-1}	934.6–1347.5
Calcic Hardness	mg $CaCO_3$ L^{-1}	487.9–675.6
Magnesium Hardness	mg $CaCO_3$ L^{-1}	296.5–709.4
Calcium	mg L^{-1}	195.6–270.8
Magnesium	mg L^{-1}	72.1–172.4
COD	mg L^{-1}	4416.7–5250.0
Turbidity	NTU	536.49–659.73
Total Phosphorus	mg L^{-1}	1796.1–4894.1
Total Phenols	mg equivalent of gallic acid L^{-1}	65.00–82.86

COD—Chemical oxygen demand.

The raw wastewater had a whitish color, solids and fats in suspension. Thus, cheese whey wastewater presented turbidity in the range of 536.49–659.73 NTU. Cheese whey wastewater exhibited pH in the range of 4.162–4.675. Similar results were obtained by Gavala et al. [7], Martins et al. [18] and Rivas et al. [11]. A conductivity range of 4.86–5.54 dS m^{-1} was noticed by raw cheese whey wastewater.

Cheese whey wastewater is a resilient organic effluent with COD values in the range of 4416.7–5250.0 mg L^{-1}. These values were higher than those obtained by Fang [8]. Raw wastewater had nutrients in its composition, such as total phosphorus (1796.1–4894.1 mg L^{-1}), calcium (195.6–270.8 mg L^{-1}) and magnesium (72.1–172.4 mg L^{-1}). Bicarbonates and calcium contents are responsible for alkalinity and hardness, respectively.

3.2. Chemical Oxidation with Hydrogen Peroxide Alone

Chemical oxidation has been applied for the treatment of water and wastewater using different reagents, including hydrogen peroxide in combinations, ozone, chlorine dioxide, sodium hypochlorite, and potassium permanganate. However, the application of hydrogen peroxide alone has rarely been reported. Oxidation with hydrogen peroxide presents several advantages, namely, simplicity of application. This oxidant can reduce organic and inorganic contaminants in industrial wastewater. Thus, in this work, different doses of hydrogen peroxide were applied for the treatment of cheese whey wastewater in order to eliminate total phenols, total phosphorus and turbidity. Furthermore, the effect of the oxidation process under different concentrations of H_2O_2 on pH, conductivity, characteristic absorbances, calcic and magnesium hardness, alkalinity and COD was also studied.

3.2.1. Total Phenols Removal

The effect of oxidation process with hydrogen peroxide on the removal of total phenols is presented in Figure 1. In general, low concentrations of oxidant (1–3 g L^{-1}) allowed the total phenols removal above 30%. Similar results were obtained for a concentration of oxidant of 5 g L^{-1}. High concentrations of oxidant (4, 6 and 7 g L^{-1}) led to the reduction of the elimination of total phenols. In such cases, removals of 17–23% were obtained. The lower removal of total phenols at high concentrations may be due to the consumption of hydrogen peroxide by the radicals formed during the oxidation process. Similar results were obtained by Madeira et al. [29] when treating slaughterhouse wastewater with oxidation processes.

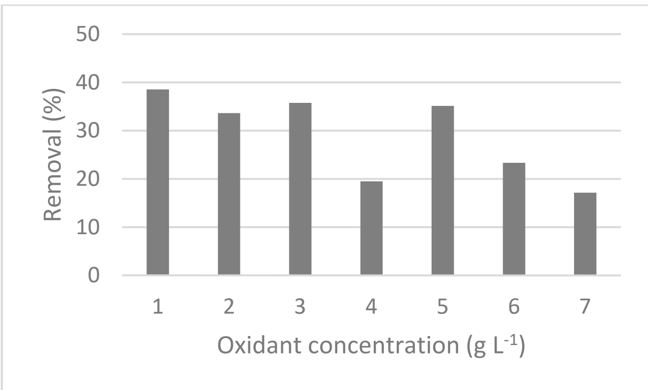

Figure 1. Effect of hydrogen peroxide oxidation on the removal of total phenols.

3.2.2. Total Phosphorus and COD Removal

The effect of oxidation process with hydrogen peroxide on the removal of total phosphorus is displayed in Figure 2. Oxidation with hydrogen peroxide led to the reduction of total phosphorus in the range of 46–53%, regardless of the dose applied (1–7 g L^{-1}). In this work, COD was recalcitrant to hydrogen peroxide. In contrast, Ksibi [30] obtained the reduction of COD, offensive odor and foaminess by increasing dose of hydrogen peroxide.

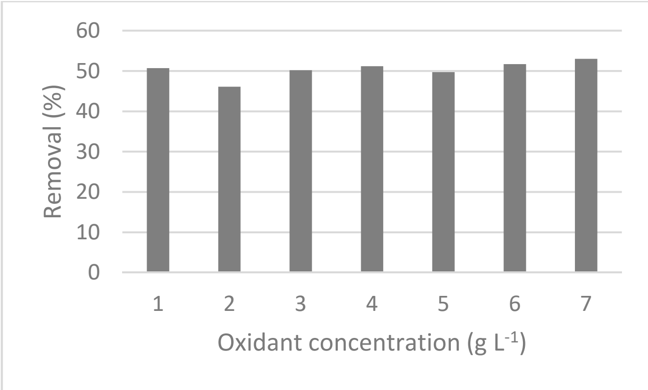

Figure 2. Effect of hydrogen peroxide oxidation on the removal of total phosphorus.

3.2.3. Turbidity Removal

The effect of oxidation process with hydrogen peroxide on the removal of turbidity is shown in Figure 3. The application of low concentration of oxidant (1 g L^{-1}) led to the reduction of 68%. The increase of oxidant doses (2–3 g L^{-1}) dealt with rise of turbidity removal in the range of 89–90% due to the action of hydroxyl radicals coming from the oxidation process. However, when increasing the concentration of oxidant to values in the range 4–6 g L^{-1}, a reduction in the elimination of turbidity (75–79%) was observed. At high concentration (7 g L^{-1}), a high efficiency (91%) of the removal of turbidity was achieved.

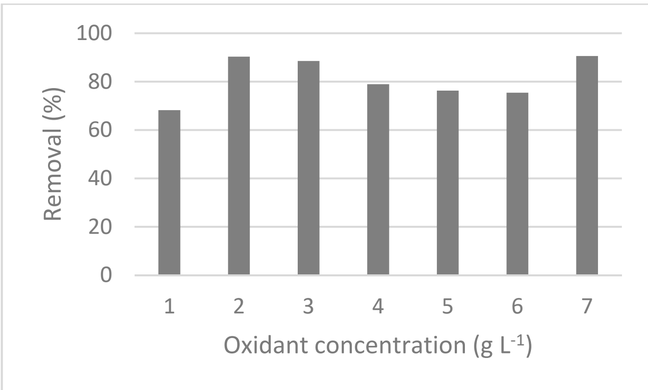

Figure 3. Effect of hydrogen peroxide oxidation on the removal of turbidity.

3.2.4. Characteristic Absorbances Removal

The effect of oxidation process with hydrogen peroxide on the removal of characteristic absorbances is presented in Figure 4. The application of low concentration of oxidant (1, 2 and 3 g L^{-1}) led to the elimination of absorbance at 220 nm in the range of 12–19%. Notwithstanding, the increase of oxidant doses (≥4 g L^{-1}) dealt with the increase of low molecular weight compounds (simple molecules) (7–22%) formed from complex molecules (humic acids). This effect can be explained through the breaking of bonds in complex molecules due to the action of hydrogen peroxide and its radicals. The application of oxidant concentration of 2 g L^{-1} induced to the increase of the removal of absorbance at 254 nm (56%), decreasing until an oxidant concentration of 5 g L^{-1} (26%). From this point, the removal maintained practically constant (24–27%). Reduction of substituents of the aromatic rings was obtained by Zouari [31] when treating olive oil mill effluent by oxidation with hydrogen peroxide. The reduction of absorbance at 410 and 600 nm presented similar behavior. Thus, the application of 2 g L^{-1} increased the absorbances removal (81–83%), decreasing until an oxidant concentration of 6 g L^{-1}. At high concentration (7 g L^{-1}), a high efficiency (80–83%) in the removal of absorbances at 410 and 600 nm was succeeded. Ksibi [30] also obtained the reduction of microorganisms (number of total coliforms) by increasing the concentration of oxidant.

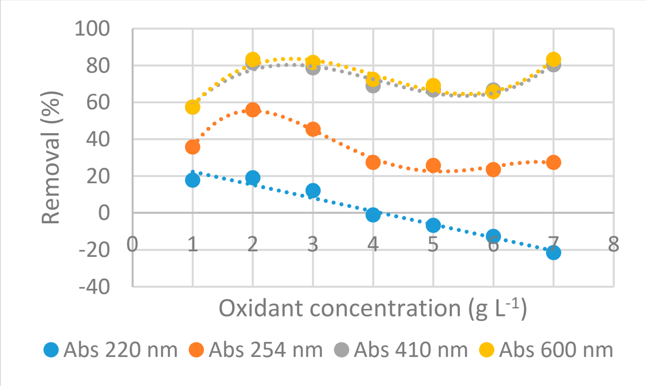

Figure 4. Effect of hydrogen peroxide oxidation on the removal of absorbances.

3.2.5. Bicarbonates Concentration

Phenolphthalein alkalinity and alkalinity to methyl orange were determined. The alkalinity was present in the form of bicarbonates. The effect of oxidation process with hydrogen peroxide on the concentration of bicarbonates is shown in Figure 5. The application of low concentration of oxidant (1 g L^{-1}) generated a treated effluent with bicarbonates concentration of 850.1 mg L^{-1} $CaCO_3$, reducing the concentration to values of 677.8 mg L^{-1} when using 2 g L^{-1} of oxidant. From oxidant concentration ≥3 g L^{-1}, the oxidation system produced a treated effluent with bicarbonates concentration in the range of 965.0–1079.8 mg L^{-1} $CaCO_3$.

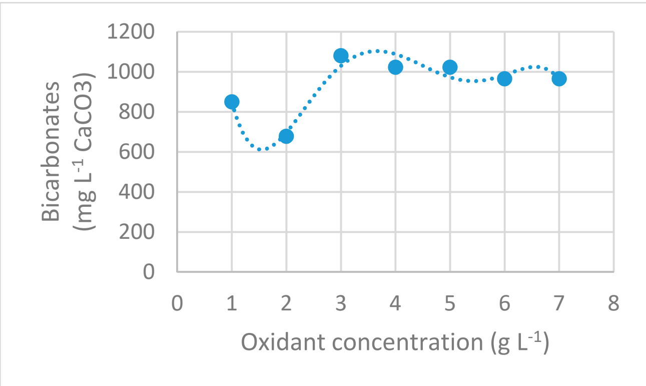

Figure 5. Effect of hydrogen peroxide oxidation on the concentration of bicarbonates.

3.2.6. Calcium and Magnesium Concentration

The effect of oxidation process with hydrogen peroxide on the concentration of calcium and magnesium is exhibited in Figure 6. The magnesium concentration remained practically constant (126.8–149.6 mg L^{-1}). At low oxidant concentrations (1, 2 and 3 g L^{-1}), oxidation system brought the high calcium removal (52–55%), producing a treated effluent with a calcium concentration in the range of 105.3–112.8 mg L^{-1}. When applying high concentrations of oxidant (≥4 g L^{-1}), the calcium removal decreased to values in the range of 20–27%, generating a treated effluent with calcium concentration in the range of 173.0–188.0 mg L^{-1}.

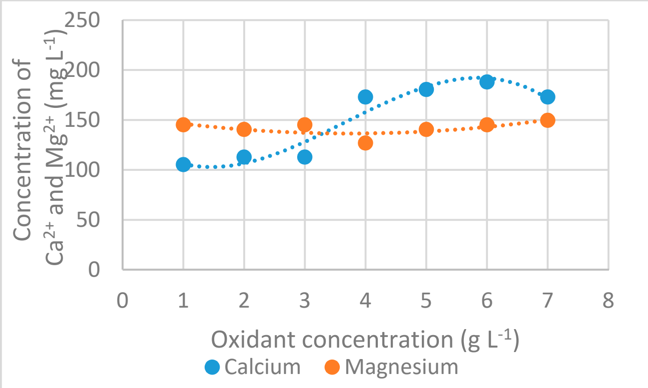

Figure 6. Effect of hydrogen peroxide oxidation on the concentration of calcium and magnesium.

3.2.7. pH and Conductivity

The effect of oxidation process with hydrogen peroxide on the pH and conductivity is exposed in Figure 7. Oxidant concentrations higher than 5 g L^{-1} induced a small reduction in conductivity and pH. Treated effluent presented values of pH and conductivity in the ranges of 4.23–4.34 and 4.86–4.98 dS m^{-1}, respectively.

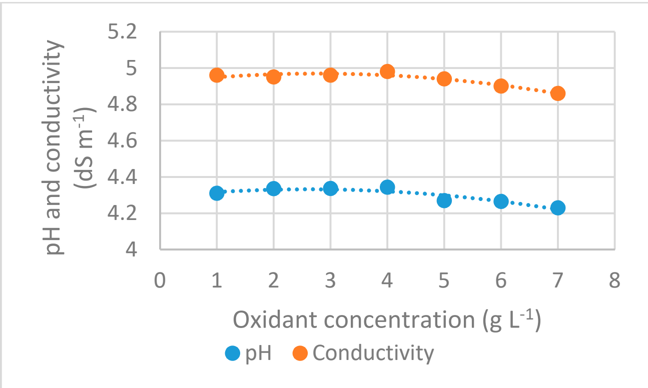

Figure 7. Effect of hydrogen peroxide oxidation on the pH and conductivity.

4. Conclusions

Cheese whey wastewater is a strong effluent in terms of salinity, acidity, phenolic, nutritional and organic contamination. Thus, the present work investigated a simple process for the treatment of cheese whey wastewater using hydrogen peroxide oxidation alone. Oxidation system was able to reduce characteristic absorbances at 220, 254, 410 and 600 nm, calcium, turbidity, total phenols and total phosphorus. Treated effluent can be post-treated by biological processes or reused for agricultural purposes.

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