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Development of a process for the treatment of fish processing saline wastewater

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ABSTRACT

In recent years, there has been a great development of fish industries in coastal countries. The wastewaters generated from such industries have an important organic load which reaches 4,000 mg/L of chemical oxygen demand (COD) and high salt concentration with a TDS of about 60 g/L. In order to reduce the organic load of these effluents, a physico-chemical process by coagulation/flocculation was coupled with a biological process. The pretreatment by coagulation/flocculation showed great performance resulting in the removal of 60 and 84% of COD and turbidity, respectively. However, the combined treatment (physico-chemical and biological process) achieved high-performance degradation of the organic load corresponding to the removal of 85% of total organic carbon (TOC) for the first effluent E1 of high salinity (55 g/L) and the removal of 96% of TOC for the second effluent E2 of relatively high salinity (18 g/L).

Keywords: High salt concentration; Organic load; Coagulation/flocculation; Biological process

1. Introduction

In recent years, there has been rapid growth of fish industries throughout the world. The fish industries in Tunisia are one of the most important sectors exceeding 100 units located on the Tunisian coast. These industries generate large wastewater volumes, generally exceeding 500 m^3/day. The volume of these wastewaters depends mainly on the raw fish composition, additives used, and processing water source [1]. These wastewaters are characterized by a high pollutant load of about 3,500 mg/L in terms of COD containing organic contaminants in soluble and colloidal form. The level of total soluble COD varies largely according to the factory and fish type [1]. Moreover, fish processing wastewaters are saline in nature which contains high salt concentration with a TDS of about 60 g/L. The high salt concentrations pose a major problem regarding their evacuation through the public sewers, because it disrupts the

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functioning of the biological treatment plant and causes the disintegration of cells by plasmolysis [2].

Saline effluents are often treated by physico-chemical processes that are used in the first stage for treating the organic matter and the salts contained in these effluents [3]. Coagulation/flocculation is one of the most used water effluent treatments. It is often used as the most effective pretreatment physico-chemical techniques [4].

Biological treatment of saline wastewater has been investigated in different systems by different researchers. Anaerobic processes such as upflow anaerobic sludge blanket reactor, anaerobic filter (AF), and anaerobic fluidized bed reactor can achieve removal of high organics (80–90%) and produce biogas. Aerobic processes such as activated sludge, rotating biological contactor, trickling filter, and lagoons are also suitable for removal of organics [1]. However, major problems are encountered in biological treatment of saline wastewater [5]. High salt content in these wastewaters reduces the treatment efficiency of conventional microbiological treatment processes of chloride concentrations exceeding 5–8 g/L [6]. Indeed, salt content in wastewater tends to increase the suspended solids in effluents due to its lysis effects which reduce the populations of protozoa and filamentous organisms [5]. Therefore, the performance obtained by a biological process depends on the biomass proper adaptation or the use of halophilic micro-organisms [7].

Several studies showed great interest in halophilic micro-organisms in the saline wastewater biological treatment [8]. Moreover, the use of halophilic microbial consortium or even the enrichment of the effluent by classic flora already adapted to saline conditions reduces the effect of salt stress on bacterial metabolism [9,10]. In fact, halophilic micro-organisms maintain an osmotic balance of their cytoplasm with the external medium by accumulating high concentration of various organic osmotic solutes [11]. Thus, the use of salt-tolerant micro-organisms in a biological wastewater treatment process could be a solution for COD removal from saline wastewater.

This study aims to develop a combined treatment process that involves the coupling of coagulation/flocculation process and the biological process by the application of halophilic consortium at different salt concentrations in order to have a better treatment efficiency of the saline effluents.

2. Materials and methods

2.1. Wastewater sampling

The effluent used in this work is an industrial wastewater generated from a fish industry located in the industrial area of Madagascar in Sfax (Tunisia). The sampling was carried out during the period corresponding to the conservation of octopus and cuttlefish. For conservation, the sample was placed at 4˚C to avoid its decomposition.

2.2. Analytical techniques

The measurements of pH, turbidity, COD, (biological oxygen demand) BOD_5, total organic carbon (TOC), dry matter, suspended solids (SS), and total Kjeldahl nitrogen (TKN) were performed according to standard methods for the Examination of Water and Wastewater [12]. Concretely speaking, measuring the dry matter consists of drying a known volume of the sample in an oven at 105˚C until the weight stabilization. The COD is determined by the acidic oxidation of organic and mineral matter present in the effluent, using potassium dichromate at a temperature of 150˚C for 2 h. However, the high chloride concentration of this effluent does not allow their complexation and makes this protocol unreliable. Thus, we adopted a different protocol for the measurement of COD [13] making the blank solutions with a chloride concentration similar to those of the samples to compensate for the chloride-induced error. BOD_5 is determined by the manometric method with a respirometer and incubation for five days. TOC is determined by combustion at high temperature (800–900˚C); CO_2 released is detected by means of an infrared sensor.

2.3. Coagulation/flocculation

Coagulation/flocculation experiments were carried out using the conventional Jar Test equipment in six beakers of 500 ml in volume at room temperature. The chemical reagents used were aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$) as a coagulant which was in powder form with a particle size of 0.1–3 mm and the Praestol as a flocculant which was in the form of white granules having a particle size of up to 1.2 mm. The experimental process consisted of three subsequent phases [14]. They are as follows:

The aluminum sulfate and Praestol solutions were prepared at a concentration of 10 g/L and 5 g/L, respectively. Flash mixing started at 150 rpm and lasted 3 min during the coagulant addition and dispersion with dosage values of 200, 400, 600, 800, and 1,000 mg/l. These dosage values were selected according to the value of turbidity. A flocculation process was conducted for 30 min by slow stirring at a rotational speed of 60 rpm. Thereafter, a settlement for three hours was performed.

2.4. Biological treatment

Batch cultures were prepared in 500-ml Erlenmeyer flasks containing 250 ml of effluent already neutralized and inoculated with a halophilic consortium cultivated under aseptic conditions in the laboratory of Environmental Bioprocess in the Centre of Biotechnology of Sfax. These cultures were incubated in a rotary shaker for four days at room temperature with stirring at 200 rpm to maintain the bacterial consortium in aerobic conditions. Three successive series of batches were carried out with two effluent types: raw and treated by coagulation/flocculation. Samples were withdrawn each day to determine the pH and the TOC.

3. Results and discussion

3.1. Characterization of the effluent

The characterization of the effluent generated from fish industries depends on some factors related to its variability over time. A sampling campaign was carried out during a period of 20 days corresponding to the conservation of octopus and cuttlefish. Table 1 illustrates the effluent average composition. The pollution load was determined by a relatively high COD of approximately 1,400 mg/L, an important value of TOC which is around 500 mg/L and high levels of nitrogen. Also, this effluent shows high salt concentrations reaching a level of 50 g/L, which are mainly due to the use of saline water for washing and packaging seafood. The importance of turbidity and the high content of suspended matter prove the important load colloidal particles present in the effluent such as the cuttlefish ink particles. The COD/BOD_5 ratio equal to two indicates the possibility of the effluent organic matter biodegradation.

Table 1
Average composition of saline wastewater from fish industry

Parameters	Values
pH	6.6 ± 0.08
Suspended solids (g/L)	0.82 ± 0.07
Dry matter (g/L)	61.44 ± 0.3
Mineral matter (g/L)	50.31 ± 0.41
Salinity (g/L)	52.17 ± 1.85
Volatile matter (g/L)	11.13 ± 0.12
TOC (mg/L)	462 ± 7.2
COD (mg O_2/L)	1,348 ± 266.3
BOD_5 (mg O_2/L)	667 ± 144
Turbidity (NTU)	206 ± 11
TKN (mg/L)	206 ± 12

3.2. Treatment by coagulation/flocculation

The efficiency of the coagulation/flocculation process depends on many factors, such as the concentration of the reagents (coagulant and flocculant), the solution pH, the speed, and stirring time. The optimization of these parameters was based on monitoring the removal of COD and turbidity. Experiments were first carried out using the suitable speed and stirring time.

3.2.1. Optimization of pH

The pH optimization was carried out by following the removal evolution of turbidity at different pH and different doses of aluminum sulfate. Fig. 1 shows that the best performance of the turbidity reduction occurs at pH 7. In fact, it was found that an increase in the solution pH resulted in an increase in the retention of aluminum sulfate particles. Thus, for pH values above 6.5 (corresponding to the pH of the raw effluent), there is a marked improvement and significant removal of turbidity (reaching up to 98%), especially for basic pH. This is due to the van der Waals dispersive forces establishing hydrogen bonds between $Al(OH)_3$ and colloidal particles [15]. Whereas, at pH 4, there is a small removal of the turbidity due to the solubility of aluminum (Al^{3+}) whose hydrophilicity reaches its maximum. On the other hand, it was found that at pH 7, the most effective turbidity removal occurs when the concentration of aluminum sulfate ranges between 0.4 and 0.8 g/L.

3.2.2. Optimization of the aluminum sulfate concentration

The optimal aluminum sulfate concentration is determined by using different doses ranging from 0.4 to 0.8 g/L with pH 7.

The correlation between the pH of the supernatant and the dose of aluminum sulfate is shown in Fig. 2. The supernatant pH values were decreased with the increase of coagulant dosage which could reflect the coagulant acidic nature [16]. The pH values range from 6.8 for a dose of 0.4 g/L to 6.4 for a dose of 0.8 g/L. In addition, the effect of aluminum sulfate dose on COD removal is illustrated in Fig. 2. A significant removal of the organic load could be observed from the dose of 0.7 g/L which reaches 33%. More studies have proved that the COD removal is associated with removal mechanisms of humic substances, which are eliminated by the addition of coagulants [17]. Indeed, the elimination of these substances is carried out by their adsorption on aluminum hydroxide

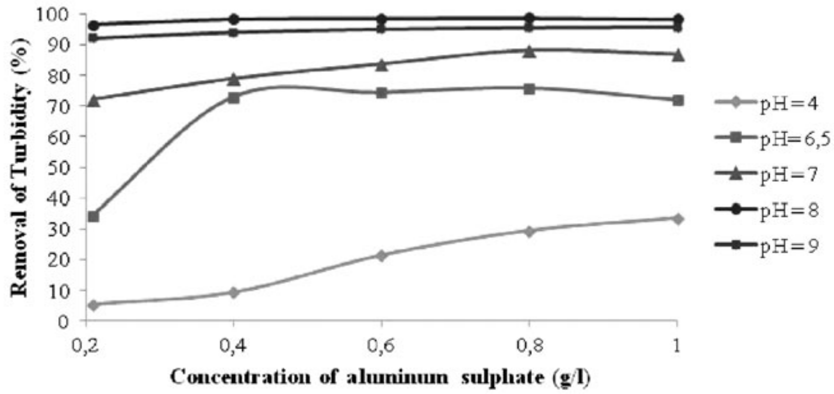

Fig. 1. Removal of turbidity of saline effluent from fish industry as a function of aluminum sulfate dosage at different solution pH.

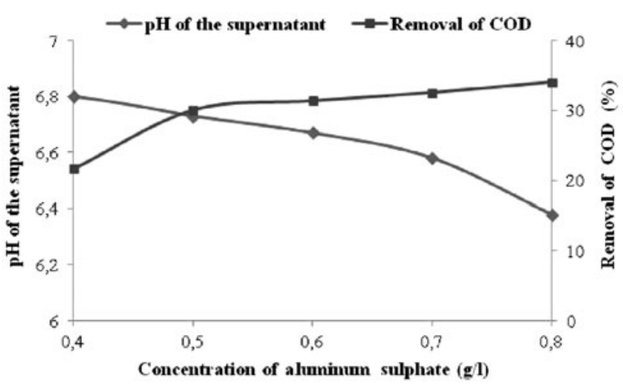

Fig. 2. Removal of COD and changes of pH of the supernatant of saline effluent from fish industry as a function of aluminum sulphate dosage.

precipitates [18]. The decolorization of the effluent as a function of coagulant dosage is illustrated in Fig. 3. As shown, a clear degradation of organic matter corresponds to the peak at the wavelength of 254 nm, which indicates the presence of aromatic organic compounds as well as other unsaturated ones [19]. This degradation is based on the dose of aluminum sulfate of 0.7 and 0.8 g/L.

The determination of the dissolved aluminum concentration in the supernatant is an essential parameter to consider because aluminum is toxic and can inhibit the activity of biomass in the effluent. Fig. 4 illustrates the residual aluminum low concentration in the dose of 0.7 g/L.

3.2.3. Optimization of the concentration of Praestol

The optimization tests were performed in the same conditions as mentioned above (pH 7 and a

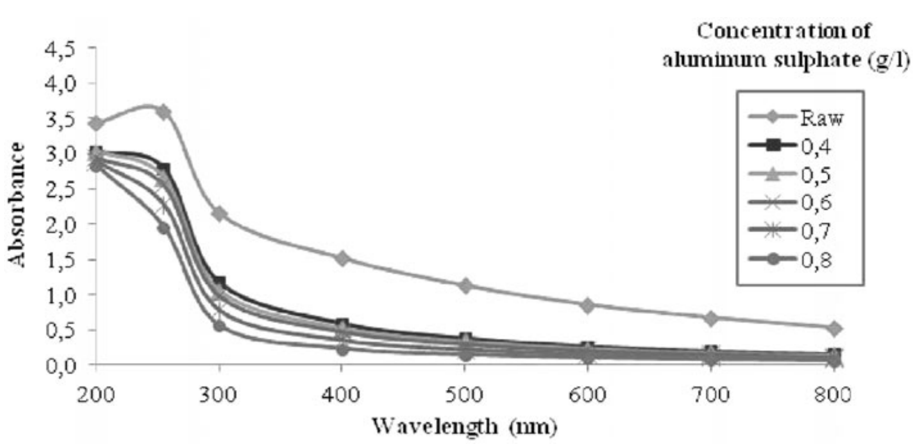

Fig. 3. Changes in the absorbance spectrum of the UV–visible of the treated saline effluent from fish industry as a function of aluminum sulfate dosage.

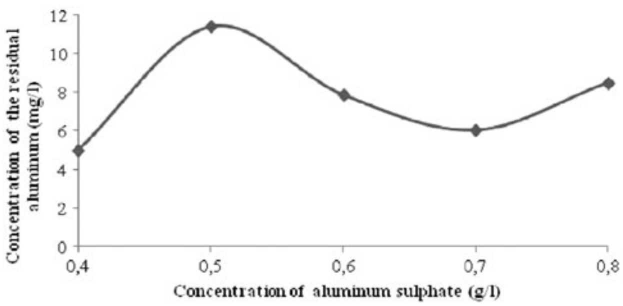

Fig. 4. Changes in the concentration of the residual aluminum as a function of aluminum sulphate dosage.

Table 2
Organic load removal of saline wastewater from fish industry after pretreatment by coagulation/flocculation

Parameters	Rate removal (%)
Turbidity	84
Suspended solids	70
Mineral matter	5
COD	60
TOC (mg/L)	45
COD (mg O_2/L)	60
TKN (mg/L)	38
$N_{organic}$	51

concentration of 0.7 g/L of aluminum sulfate) using different concentrations of Praestol ranging from 5 to 50 mg/L and based on monitoring turbidity and COD removal. Fig. 5 illustrates a better performance of flocculation. As seen, at a concentration of 50 mg/L, removal rate achieved 90% of turbidity, and 61% of COD. However, for economic reasons, a concentration of 10 mg/L was chosen as an optimal concentration which reaches 84% and 60% for the turbidity and COD removal, respectively.

Summarizing the aforementioned results, the pretreatment of the effluent generated from fish industries by the application of coagulation/flocculation process resulted in the efficient removal of organic and polluted load as indicated by the experiments presented in Table 2.

3.3. Biological treatment batch

The high salinity and relatively the high pollution load of this effluent make the conventional microbiological treatment processes difficult. Therefore, a phase of acclimatization is performed in batch, in aerobic conditions at room temperature. The effluent is inoculated with a halophilic consortium. Thus, this step allows the selection of bacteria that may adapt to pollution in the presence of high salt concentrations. In our case study, two different salinity effluents were chosen: the first (E1) had a salinity of 55 g/L, whereas the second (E2) had a salinity of about 18 g/L. The pretreatment of these effluents by the process of

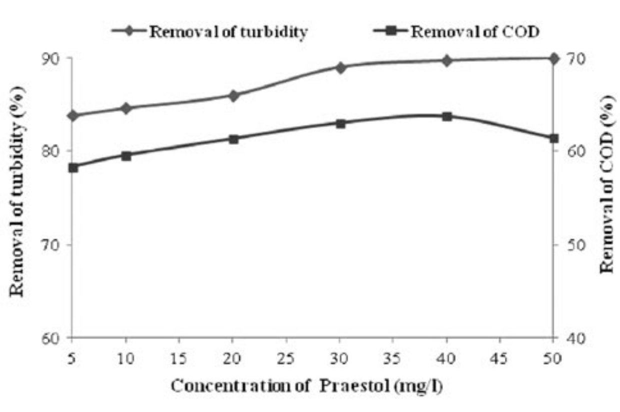

Fig. 5. Removal of COD and turbidity of saline effluent from fish industry as a function. of Praestol dosage with a concentration of 0.7 g/L of aluminum sulphate at pH 7.

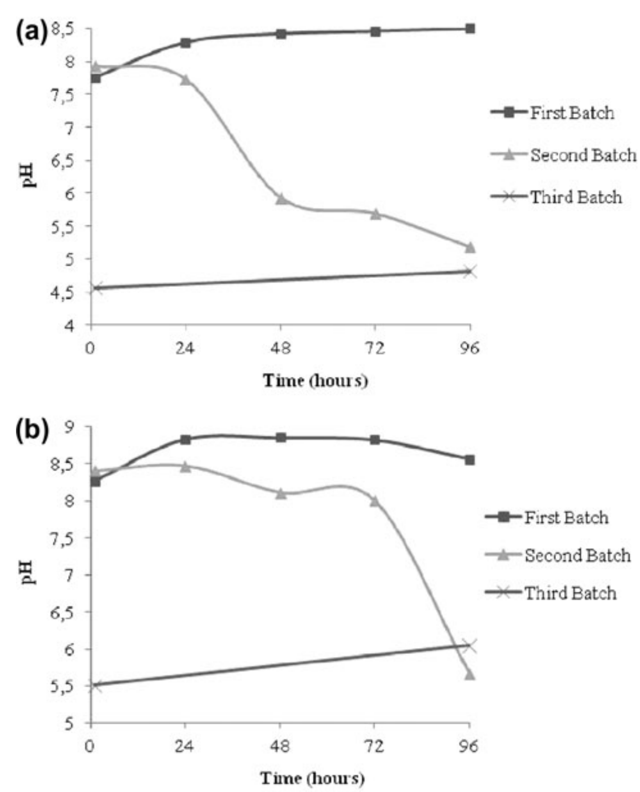

Fig. 6. Evolution of pH over time for the raw effluents E1 (55 g/L) (a) and E2 (18 g/L) (b) in three series of batches.

coagulation/flocculation allowed the production of two by-products which were: T1 corresponding to the pretreatment of effluent E1 and T2 corresponding to the pretreatment of effluent E2.The tests were carried out in three successive series of batches in which each series represented the four types of effluents: E1/E2/T1/T2. The acclimatization of the biomass, characterized by a dominance of halophilic bacteria, was carried out by monitoring two physico-chemical parameters in the effluents: the solution pH and the TOC.

3.3.1. Evolution of pH

Fig. 6 shows almost the same trends in the evolution of pH for both raw effluents E1 and E2. In the first batch, the pH tends to increase to stabilize at around 8.5 thus demonstrating the suitability of bacteria. However, from the second batch, the pH decreases drastically to become in the third batch acidic pH of 4.8 for effluent E1 with high salinity of 55 g/L (Fig. 6(a)) and 5.7 for effluent E2 with salinity of 18 g/L (Fig. 6(b)). During these tests, the biological acidification might be explained by the development of certain fungi tolerant to the mid acidity due to the emission of acids during biodegradation [20].

Unlike for effluents T1 (51 g/L) and T2 (17 g/L), the pH of the biological mid remains alkali with a slight gradual increase from the first to the second batch. From the third batch, the pH has a tendency to decrease to a value of 7.8 for effluent T1 and a value of eight for effluent T2 (Fig. 7). This alkaline mid proves the efficiency of the biological activity confirmed by a highly significant removal of TOC as shown in Fig. 8. Moreover, some authors have shown that the decarboxylation of organic acids in saline environments is manifested by alkalinization of the mid [21].

3.3.2. Evolution of total organic carbon (TOC)

Experiments of biological treatment of raw effluents (E1 of 55 g/L and E2 of 18 g/L) showed a gradual removal of TOC over time. The removal of the organic load was based on the sequence of batches and essentially the difference in salinity between both effluents E1 and E2 (Fig. 8). Indeed, in the third batch, there was a small removal of TOC reaching 40% for effluent E1 (Fig. 8(a)) and 51% for effluent E2

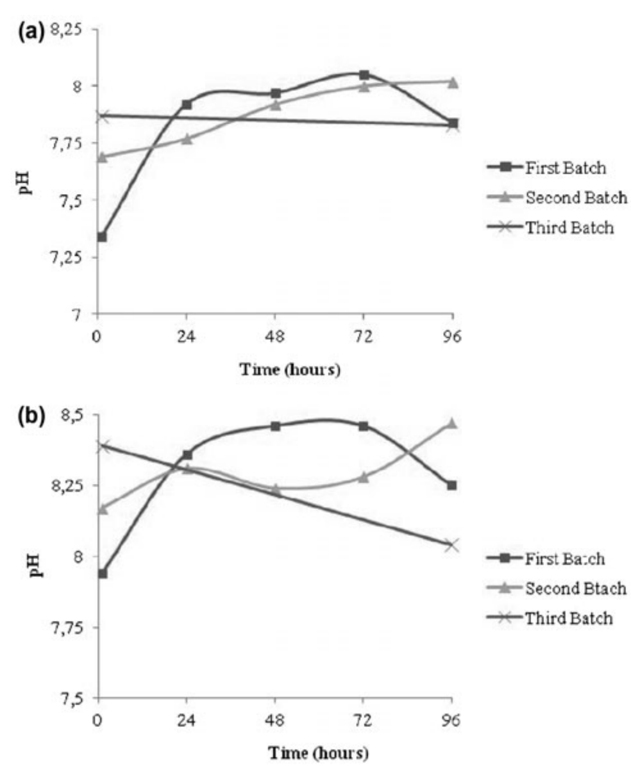

Fig. 7. Evolution of pH over time for the treated effluents T1 (51 g/L) (a) and T2 (17 g/L) (b) in three series of batches.

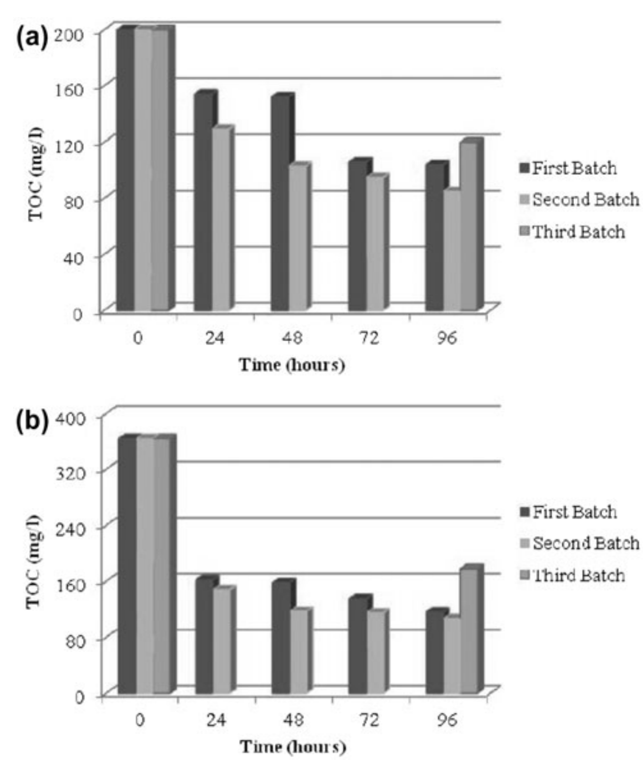

Fig. 8. Evolution of TOC over time for raw effluents E1 (55 g/L) (a) and E2 (18 g/L) (b) in three series of batches.

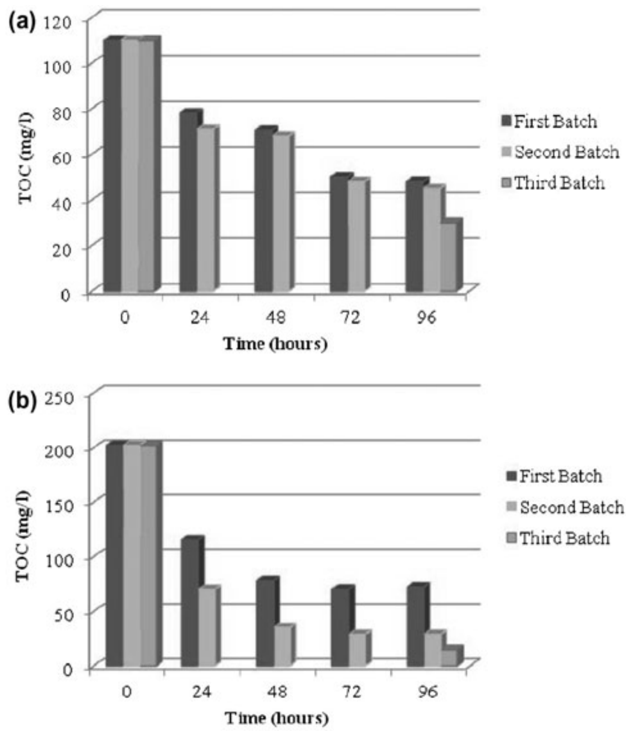

Fig. 9. Evolution of TOC over time for treated effluents T1 (51 g/L) (a) and T2 (17 g/L) (b) in three series of batches.

(Fig. 8(b)). This shows the difficulties of adaptation of the micro-organisms to the effluent due to the high organic load present and the mid salinity.

However, as regards pretreated effluents by coagulation/flocculation, the efficiency of TOC removal was very important especially in the third batch. Indeed, for effluent T1 of salinity equal to 51 g/L, the maximum removal of TOC achieved was 85% (Fig. 9(a)) while in the case of effluent T2 of salinity equal to 17 g/L, the maximum removal of TOC was 96% (Fig. 9(b)). Thus, the biological treatment coupled with batch process of coagulation/flocculation has great performance in the elimination of the organic load in the effluent.

4. Conclusions

Our study aims to reduce the organic load of saline wastewater from fish industries. The pretreatment by coagulation/flocculation has been optimized at neutral pH with a concentration of 0.7 g/L of aluminum sulfate as a coagulant and 10 mg/L of Praestol as a flocculant. This pretreatment shows great performance resulting in a removal of 60% of COD and 84% of turbidity. The second step of this work is to treat the effluent by a biological process to further reduce the pollution load. The process consists in inoculating the effluent by a halophilic consortium to adapt to excessive concentrations of salts. The experiments were concerned with two raw effluents and then their pretreated effluents by coagulation/flocculation. Three series of successive batches were performed on each type of effluent. As for the raw effluents, the results show a removal of 40% regarding the high effluent salinity of 55 g/L and a removal of 51% regarding the effluent with a relatively high salinity of about 18 g/L. However, the combined physico-chemical and biological treatment achieved high-performance degradation. The results show a removal of 85% of TOC with a value of 30 mg/L for the effluent with high salinity (55 g/L) and a removal of 96% with a value of 15 mg/L for the effluent having a salinity of 18 g/L.

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